ORGANOTIN COMPOUNDS IN THE AQUATIC ENVIRONMENT:

SCIENTIFIC CRITERIA FOR ASSESSING THEIR EFFECTS ON ENVIRONMENTAL QUALITY

BY

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PANEL ON ORGANOTIN COMPOUNDS IN THE AQUATIC ENVIRONMENT

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SUMMARY

Sources (see Chapter 2)

Organotin compounds are currently one of the most studied organometallic systems in terms of industrial and agricultural applications. The two most important industrial applications are as stabilizers and catalysts. Sulfur-containing mercaptide compounds (e.g. dibutyltin bis(isooctyl mercaptoacetate)) are used for heat stabilization of poly(vinyl chloride) polymers, whereas nonsulfur compounds (e.g. dibutyltin dilaurate) impart light stability. Diorganotin compounds are also useful as catalysts in the production of polyurethane foams and in the room-temperature vulcanization of silicone rubbers.

The biocidal uses of organotin compounds were first discovered in the 1950's; since that time, the major organotin biocides (e.g. bis(tributyltin) oxide, tributyltin fluoride, triphenyltin hydroxide and tricyclohexyltin hydroxide) have found use as agricultural fungicides, bactericides, preservatives for wood, textiles, paper, leather and electrical equipment, insecticides, acaricides, anthelmintics and molluscicides. Their most significant biocidal application in terms of environmental contamination is without a doubt as antifouling agents in paints, to prevent the adherence of microorganisms, plants and animals to the bottoms of ships and to other surfaces immersed in seawater.

The total annual Canadian market (production and import) for organotin compounds has been estimated to exceed 1 x 10^6 kg. Of the 10 or so organotin compounds used in Canada in large amounts, only dibutyltin dilaurate and stannous 2-ethylhexanoate (which is not a true organotin compound) are manufactured here. The remainder (about 90% of organotin compounds used) is presumably imported. None of the organotin compounds produced in Canada is exported.

The Canadian market is dominated by dibutyltin bis(isooctyl mercaptoacetate), used in the manufacture of poly(vinyl chloride) products. The major end uses for organotin compounds in Canada are as poly(vinyl chloride) stabilizers (an estimated 80-82%), catalysts (16-17%), and biocides (2-3%). Many companies in Canada have registered, under the Pest Control Products Act, commercial and domestic products that contain organotin compounds; some examples of compounds used for crop protection are triphenyltin hydroxide (Du-Ter) and tricyclohexyltin hydroxide (Plictran).

Little, if any, information exists concerning the amounts of organotin compounds entering the Canadian aquatic environment by the production, processing, use or disposal routes. Only one manufacturing location for organotin compounds, specifically dibutyltin dilaurate, is known to exist in Canada; losses to the environment during production and disposal are unknown. Quantities released by facilities using organotin compounds in the production of, for example, poly(vinyl chloride) resins, are also not known. Industrial and consumer disposal of organotin compounds that have been used as stabilizers, catalysts, biocides and preservatives may also result in environmental exposure, although the impact of the disposal methods, usually sanitary landfill or incineration, is again unknown.

Although the major use of organotin compounds in Canada is in the area of heat stabilization, the greatest potential for direct contact with the environment is from biocidal applications. Organotin compounds used in biocidal paints and preservatives, for example, may leach into the water during their use, particularly in the vicinity of docks and marinas. Organotin compounds used in crop protection in Canada may also enter the environment during use, although this is probably not a significant route because of the limited acreage treated and the high air dilution factor.

Chemistry (see Chapter 3)

For the purposes of this document, an organotin compound is defined as one containing a tin-to-carbon bond. The formula R_nSnX_{4-n} (n = 1-4; R = alkyl or aryl; X = H, OR', halogen, etc.) is used to symbolize known compounds. The symbol Q, as in R_nSnQ_{4-n}, is used where only R is known.

In this chapter, the formation and cleavage of tin-carbon bonds are discussed, and the chemistry of compounds with tin-halogen, tin-pseudohalogen, tin-oxygen, tin-sulfur, tin-nitrogen, tin-hydrogen and tin-metal bonds, as well as organotin esters, is briefly outlined. Reactions and properties of environmental and analytical significance are emphasized. Synthetic routes to compounds used commercially are also delineated. The properties of selected organotin compounds are tabulated in Appendix III.0.

Analytical Approaches (see Chapter 4)

The analytical chemistry of organotin compounds dates back to the mid-1920's, at which time the organotin compound was first degraded in mineral acids to the inorganic form, then analyzed. Since that time, emphasis has been placed on the development of techniques that can be used in the direct analysis of the various chemical forms of organotin compounds at environmental concentrations. Spectrophotometric, spectrofluorimetric, and electrochemical techniques, including polarography and anodic stripping voltammetry, may be applied to the determination of organotin compounds in aqueous media. However, these methods are not sensitive enough to determine concentrations of organotin compounds in natural water in the picomole per litre range.

Instead, combination methods involving separation of the organotin species and element-specific detection are more commonly employed. For example, gas chromatography may be used in conjunction with atomic absorption or emission spectrometry, flame photometry, hydrogen flame ionization, electron capture, and mass spectrometry for the determination of organotin compounds in aqueous media.

For the initial gas chromatographic separation of the organotin compounds, the analytes must be volatile or rendered volatile by a derivatization technique. In hydridization, excess borohydride reagent is used to convert the cationic alkyltin species to the corresponding hydrides, R_nSnH_{4-n}, which are then purged from solution with an inert gas and collected in a cold trap. Rearrangement of the alkyl groups often obscures the original speciation. The second derivatization technique involves the reaction of alkyltin species with a Grignard reagent which proceeds to completion at very low concentrations with no rearrangement of the alkyl groups.

Atomic absorption or emission has been the most widely chosen element-specific detection system for use with gas chromatography. The atomization device is usually an electrically heated graphite furnace or a quartz tube furnace. The flame photometric detector is the most sensitive detector used for the gas chromatographic analysis of organotin compounds, especially when the model has a glass internal surface. Detection limits are now as low as 5×10^{-18} mol tin per second. Detector sensitivity, however, can be decreased by the accumulation of SnO_2 and by other compounds extracted from environmental media along with organotin species.

The liquid chromatographic separation of organotin compounds does not require the preparation of volatile analytes. It would be the method of choice for the analysis of nonvolatile or high-molecular-weight organotin compounds were it not for the fact that the development of sensitive detectors has been slower than in the field of gas chromatography. Many problems associated with using the furnace atomic absorption spectrometer together with a liquid chromatograph, as well as with solvent interferences of the plasma, still remain to be solved, but progress is being made.

All the above methods are applicable to the analysis of organotin compounds in water. The combination of separation technique and element-specific detector, such as gas or high-pressure liquid chromatography with atomic absorption spectrometry, is the obvious choice for speciation analysis of organotin compounds. There are, in contrast, few reports on the analysis of organotin compounds in sediment or biota. Much more work remains to be done in these areas.

Environmental Occurrence and Transformations (see Chapter 5)

Concentrations in Aquatic Systems (see Sections 5.1, 5.2, 5.3)

Current data on the aquatic environmental occurrence of inorganic tin and organotin compounds are contained in Appendix V.0. Very low concentrations of dissolved total inorganic tin are found in seawater, rivers and lakes, because hydrolysis products of tin are highly insoluble. Methyltin species, which can be derived from anthropogenic sources as well as from biotic and abiotic methylation of inorganic tin and organotin compounds, have been detected in a variety of natural waters, sediments, and rain. Butyltin compounds, which occur in close association with harbor locations because of their anthropogenic sources, have been found in lakes, rivers, and sediment. The concentrations of methyltin and butyltin species in the water of lakes and rivers in Ontario are tabulated in this chapter, together with concentrations of these compounds in sediments.

To date, no measurements have been made of organotin species in Canadian estuarine and marine waters. Methyltin compounds have, however, been observed in coastal regions of the United States and Turkey, with different species predominating depending on the region. Methyltin hydrides have been found in Baltimore Harbor. Butyltin species have been observed in saline waters: Baltimore Harbor (including the volatile hydride $C_4H_9SnH_3$) and a Portuguese estuary. No other organotin species (e.g. phenyl, cyclohexyl) have been reported thus far.

Persistence and Fate in Aquatic Systems (see Section 5.4)

With respect to the persistence and fate of organotin compounds in aquatic systems, some of the more important considerations are such basic properties as aqueous solubility and vapor pressure, and such processes as hydrolysis, volatilization, sunlight photolysis, adsorption to suspended matter and to sediments, and methylation/demethylation. Detailed information on the properties and transformations of inorganic tin and organotin compounds relevant to their aquatic environmental fate is contained in Appendix VII.0. This section discusses the persistence and fate of tin and organotin compounds by class, in terms of their abiotic degradative reactions.

Methylation of inorganic tin and methyltin compounds is a significant environmental phenomenon, since the process can convert tin to more volatile and more toxic forms. Several research groups have shown that inorganic tin and methyltin compounds can be methylated in nutrient medium or natural water-sediment mixtures. Various products, including CH_3Sn^{3+}, $(CH_3)_2Sn^{2+}$, $(CH_3)_3Sn^+$, $(CH_3)_4Sn$ and a methyltin hydride of unknown composition have been identified. Tributylmethyl-

and dibutyldimethyltin species have been found in harbor sediments, which suggests that some butyltin compounds may be methylated in aquatic systems. Proposed mechanisms for the methylation of tin, including methyl transfer from methyl cyanocobalamin and transmethylation, are discussed in this section.

Distribution and Degradation in Aquatic Biota (see Section 5.5)

The tendency of an organotin compound to be concentrated by an organism depends on its partition behavior between the lipid and aqueous phases. In general, the larger the number and molecular weight of organic groups attached to the tin atom, the lower the compound's solubility in water and the higher its solubility in octanol. The octanol-water partition coefficients for several organotin compounds suggest that the potential for bioaccumulation exists, particularly for those compounds whose R groups are at least as large as the butyl group.

Few workers have studied the uptake, distribution and bioconcentration of organotin compounds in aquatic organisms. In carp, the uptake of triorganotin species from water through the gills has been observed, followed by its distribution among various tissues and organs, in particular the gall bladder, which stores toxic substances in bile. Significant amounts found in the kidneys and spleen suggest that the compound may affect the hematopoietic organs of the carp. In general, the amounts of organotin compounds in the organs and tissues of carp increased with duration of exposure and concentration in the external medium. The accumulation of triethyltin species in the organic constituents of the carp's liver, brain and muscle tissue was also determined, and was found to be maximal in the glycogen of liver; large amounts in the lipid and glycogen fractions of the brain and spinal cord suggest the potential for changes in the carp's fat and carbohydrate metabolism.

The accumulation of triorganotin compounds by sheepshead minnows, goldfish, mud crabs, oysters, snails and Daphnia has also been observed. In sheepshead minnows, the maximum observed bioconcentration factors were x1810 (muscle), x2120 (head), x4580 (viscera) and x2600 (whole fish). In mud crabs fed brine shrimp labelled with ^{14}C-labelled bis(tributyltin) oxide, the hepatopancreas attained the highest concentration factor (4400) after 4 d; other tissues, including gills and testes, had concentration factors ranging from 500 to 1300. In snails exposed to ^{14}C-labelled organotin compounds, relatively high levels of ^{14}C-labelled residues found in the reproductive system and nuclear fraction may explain the low tolerance and development rate noticed in subsequent generations exposed to the compound.

Almost no work has been done on the metabolic degradation of organotin compounds by aquatic organisms, which determines in part the organism's ability to lessen their deleterious effects. In general, fish appear to metabolize at least part of the triorganotin residues to lower and less toxic alkyl moieties, as well as to inorganic tin. This agrees with findings on mammalian metabolism of triorganotin compounds.

Clearance or elimination of organotin compounds from aquatic organisms has been observed in sheepshead minnows, carp, goldfish, and oysters. In sheepshead minnows, less than 80% of ^{14}C residues from labelled bis(tributyltin) oxide had been depurated after a 28-day depuration period. The long half-life of triphenyltin residues in goldfish led to the speculation that lethal levels would be built up after a few years, even at low external concentrations of the compound.

There is very little information on organotin burdens in plant materials and virtually nothing on uptake of organotin compounds by plants. Most studies of plant and tissue burdens have dealt with total tin which may be present as organic or inorganic species. Concentrations of tin in aquatic and other plants, together with bioconcentration factors, are discussed.

Several species of algae have been found to contain tin and organotin species. Marine algae Ulva, Enteromorpha, and Sargasum spp. from Mission Bay and San Diego Bay contained butyltin as well as decreasing amounts, respectively, of mono-, di-, and trimethyltin chloride. The uptake of ^{113}Sn from labelled triphenyltin chloride in seawater by Enteromorpha intestinalis and Ulothrus flacca was found to increase in the light or in the dark, depending on the species.

Because of the widespread use of organotin compounds as antifungal agents, it is surprising that there is no published information on cellular burdens, intracellular location, or mode of uptake of tin in fungi. One report describes the degradation of tributyltin oxide by fungi to di- and monobutyltin compounds.

Several species of resistant bacteria have been found to accumulate the tributyltin moiety, bioconcentrating it up to 850 times. Uptake did not appear to be an active transport phenomenon. The tributyltin moiety seemed to be bound to the cell surface, but was not metabolized. Dimethyltin-resistant microorganisms were found to exclude the compound whereas tributyltin species and stannic chloride were taken up. Accumulation may not be an active cellular process since tin concentrations were identical in killed and viable cells. There are few additional studies examining the uptake and degradation of organotin compounds by microorganisms.

Effects on Aquatic Organisms (see Chapter 6)

In comparison with the amount of information collected on the effects of organotin compounds on mammalian systems, there is relatively little available on the effects of these toxicants (as biocides) on nontarget aquatic organisms. This information is essential if we are to find a range of concentrations of toxicant that destroy specific target organisms with minimal effects on other aquatic organisms.

Most studies to date have concentrated on short-term exposures of such organisms as frog tadpoles, freshwater and marine fish species, zoeal shore crabs, lobster larvae, amphipods, snails, clams, oysters, mussels, algae, and microorganisms, to high concentrations of trialkyl- or triaryltin compounds to facilitate calculation of LC_{50} values. These studies are reviewed in this chapter.

Predictions of Effects from Observed Levels (see Chapter 7)

Only in recent years have studies been concerned with the effects on aquatic organisms resulting from long-term exposures to low, environmentally realistic concentrations of organotin compounds. Those experiments enable us to correlate dose-effect data with observed levels of pollutant in the environment. Tributyltin compounds are the only group of organotin compounds for which there are measurements of concentrations in water as well as measurements of effects on aquatic organisms. Table i is a compilation of data from the literature relating the effects of exposures of selected aquatic organisms to low concentrations of tributyltin compounds. It is evident from the table that exposures of aquatic organisms to tributyltin concentrations as low as 200 $ng.L^{-1}$ for extended periods of time could lead to serious effects on growth, reproduction and metabolic processes. Since this and higher concentrations of tributyltin compounds have been observed in Canadian fresh waters, it is apparent that these organotin compounds could have a detrimental effect on fish and other aquatic organisms. An appropriate conclusion with respect to these compounds in marine waters cannot be reached until measurements are made of the levels of butyltin compounds in these waters.

Table 1. The effects of exposures to low concentrations of tributyltin compounds on selected nontarget aquatic organisms.

Compound	Organism[a]	Concentration		Exposure time	Comments	Location in text	Reference
		$\mu g.L^{-1}$	$nmol.L^{-1}$ Sn				
Tributyltin chloride	fish	0.4	1.2	6 weeks	effects on enzyme activities		Leeuwangh et al. (1976)
"	rainbow trout Salmo gairdneri yolk sac fry (fw)	5	15	12 d	lethal	6.4.4, 6.4.5	Seinen et al. (1981)
"	"	1	3.1	110 d	diminished glycogen storage; significant decrease in Hb concentration; growth retardation; decrease in body weight	"	"
		0.2	0.62	110 d	diminished glycogen storage; growth retardation; decrease in body weight	"	"
Bis(tributyltin) oxide, tributyltin acetate, chloride	guppy Lebistes reticulatus (fw)	21-39	65-130	7 d	50% survival	Table 6-1	Polster and Halacka (1971)
Bis(tributyltin) oxide	sheepshead minnow Cyprinodon variegatus (sw)	18	61	7 d	50% survival	Table 6-1	Ward et al. (1981)
		1	3.4	14 d	50% survival		
		0.96	3.2	21 d	50% survival		
"	"	0.18-1.0	0.61-3.4	167 d	concluded chronic toxicity not significantly greater than acute toxicity even though bioaccumulation occurred	6.4.5	"
"	North Sea sole Solea solea larvae (sw)	2.1	7.1	96 h	50% survival	6.4.1	Thain (1983)
"	teleost Agonus cataphractus (sw)	16	54	96 h	50% survival	6.4.1	"
"	4th stage lobster larvae (sw)	1-10	3.4-34		toxic	6.5.1	Jones and Millson (1982)

Table 1. (Cont'd)

Compound	Organism[a]	Concentration		Exposure time	Comments	Location in text	Reference
		μg.L^{-1}	nmol.L^{-1} Sn				
Bis(tributyltin) oxide (cont'd)	lobster *Homarus americanus* *larvae* (sw)	20	67	24 h	lethal	6.5.1	Laughlin and French (1980)
		5-15	17-51	up to 6 d	acutely toxic	"	"
		1	3.4		larvae able to metamorphose successfully (same as controls)	"	"
"	sand shrimp *Crangon crangon* *larvae* (sw)	1.5	5.1	96 h	50% survival	"	Thain (1983)
"	shore crab *Carcinus maenus* *larvae* (sw)	10	34	96 h	50% survival	"	"
"	amphiphod· *Orchestoidea californiana* (sw)	6, 10, and 15	20, 34 and 51	9 d	53, 20 and 7% survival; toxicity apparent only after 5 d of exposure, suggesting short-term toxicity tests may seriously underestimate toxicity	6.5.2.1	Laughlin *et al.* (1982)
Bis(tributyltin) oxide, tributyltin fluoride	amphipod *Gammarus oceanicus* *adults* (sw)	3	10	10-12 d	50% survival	6.5.2.1	Laughlin *et al.* (1984b)
		3	10	8 weeks	0% survival	"	"
	amphipod *Gammarus oceanicus* *larvae* (sw)	0.3, 3	1, 10	8 weeks	significant effect on larval survival	"	"
		0.3	1	several weeks	release of larvae reduced or blocked, growth of larvae exposed to bis-(tributyltin) oxide decreased significantly	"	"

Table i. (Cont'd)

Compound	Organism[a]	Concentration µg.L^{-1}	Concentration nmol.L^{-1} Sn	Exposure time	Comments	Location in text	Reference
Bis(tributyltin) oxide, tributyltin fluoride (cont'd)	harpacticoid Nitrocra spinipes (sw)	1-3	~3.2-10	96 h	initial concentration killing 50% of organisms	6.5.5	Lindén et al. (1979)
Bis(tributyltin) oxide	copepod Acartia tonsa (sw)	1	3.4	96 h	50% survival	6.5.3	U'ren (1983)
		0.75	2.5	120 h	50% survival	"	"
		0.55	1.9	144 h	50% survival	"	"
"	snail Biomphalaria glabrata (fw)	10, 1 0.1	34, 3.4 0.34		oviposition inhibited by 100%, >90%, 50%	6.7.2.5	Ritchie et al. (1974)
		10	34		newly laid eggs did not develop	"	"
		1	3.4		3% eggs hatched	"	"
		1, 0.1, 0.01, 0.001	3.4, 0.34, 0.034, 0.0034		egg laying of snails exposed continuously to toxicant after hatching significantly reduced in survivors	"	"
		1, 0.1	3.4, 0.34		growth severely retarded	"	"
"	Japanese oyster Crassostrea gigas larvae (sw)	1.6	5.4	48 h	50% survival	6.7.3.2	Thain (1983)
"	Japanese oyster Crassostrea gigas spat (sw)	0.15	0.51	56 d	decreased growth; pronounced thickening of upper shell valve	6.7.3.2	Waldock and Thain (1983)
		1.6	5.4	56 d	severe inhibition of growth	"	"

Table i. (Cont'd)

Compound	Organism[a]	Concentration µg.L⁻¹	Concentration nmol.L⁻¹ Sn	Exposure time	Comments	Location in text	Reference
Tributyltin acetate	mussel *Mytilus edulis* *Larvae* (sw)	2.3	7.7	48 h	50% survival	6.7.3.2	Thain (1983)
	Japanese oyster *Crassostrea gigas* (sw)	100	290		inhibited fertilization	6.7.3.2	His and Robert (1980)
		10	29		egg cleavage inhibited by 20%	"	"
		5	14		development inhibited	"	"
	oyster D larvae (sw)	5	14	48 h	100% mortality	"	"
"	Japanese oyster *Crassostrea gigas*; mussel *Mytilus galloprovincialis* (sw)	1	2.9		abnormal larvae formed; decreased growth	6.7.3.2	Robert and His (1981)
	Crassostrea gigas (sw)	1	2.9	12 d	100% mortality	"	"
	Mytilus galloprovincialis (sw)	3	8.6	9 d	25% mortality	"	"
Tributyltin species	adult oysters (sw)	0.2	≈0.7	113 d	30% mortality	6.7.3.2	Alzieu *et al.* (1980)
		2	≈7	30 d	100% mortality	"	"
Tributyltin chloride	alga *Euglena gracilis* *chloroplasts*	6.5	20	15 min	photophosphorylation inhibited	6.9	Kahn (1968)
Bis(tributyltin) oxide	diatom *Skeletonema costatum* (sw)	1-18	3.4-60	5 d	algistatic	6.9	Thain (1983)
"	"	>18	>60	5 d	algicidal	"	"

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[a] fw, freshwater; sw, seawater (marine).

RECOMMENDATIONS FOR RESEARCH

The evaluation of the hazard posed by organotin compounds in aquatic systems is predicated on (a) their chemical composition, (b) their concentration in any particular "compartment" (e.g. water, sediment, etc.), (c) their persistence in that compartment, and (d) their toxicity to organisms that occupy that compartment.

COMPOSITION AND CONCENTRATIONS

We recommend that a comprehensive survey of organotin species (as opposed to total tin or total organic tin) in Canadian salt- and freshwater ecosystems (sediment, water, organisms, leachates and sludges) be undertaken.

In order to implement this, better methodology is required in some areas, e.g. improvement of analytical methods for nonvolatile organotin species, and refinement of existing techniques (if possible) with regard to limit of detection versus limit of quantitation. The method involving high-pressure liquid chromatography, hydride generation, and quartz tube furnace atomic absorption spectrometry seems most promising for organotin species of low molecular weight; the detection of less volatile species, however, might benefit from the continuous coupling of a microbore high-pressure liquid chromatograph to a flame photometric detector or atomic absorption spectrometer. In particular, methods must be developed for the determination of the speciation of organotin compounds in natural waters and sediments. The development of analytical methods for tissues (especially in matrices with high lipid/protein concentrations) is also required. In addition, because tin found in plant and animal tissues may be in the form of organotin compounds, it is important to establish appropriate baseline levels.

PERSISTENCE AND MOBILITY

There is a lack of information in the open literature about the environmental persistence of organotin compounds. Knowledge concerning persistence is of prime importance because the nature and residence time of the organotin species in an environmental compartment are important factors in determining its availability to aquatic organisms.

The environmental compartments of concern are sediments and sediment interstitial waters, suspended particulates, and the water column. Sediments generally act as reservoirs for contaminants such as heavy metals, yet little work has been done on the partitioning of organotin compounds between particulates and interstitial waters. Similarly, there is little information on the partitioning of these compounds between the surface microlayer and subsurface waters.

The physical and chemical pathways that distribute the compounds to the various compartments need to be delineated. Some possible processes are:

(i) adsorption and desorption which can be related to charge on the organotin moiety as well as specific binding sites on the particulates;

(ii) photolytic processes which can result in cleavage of R and/or Q from R_nSnQ_{4-n};

(iii) methylation and dealkyl(aryl)ation processes for which the relative contributions from abiotic and biological sources have not been determined - much information on both processes is currently equivocal; and

(iv) volatilization from water - this will probably be important for tetraorganotin compounds of low molecular weight, e.g. $(CH_3)_4Sn$.

TOXICITY

Tissue Burdens

Organotin compounds are known to accumulate in certain aquatic organisms, and can be biomagnified to different extents in different tissues. Some organotin compounds, in particular trialkyl- and triaryltin compounds, are toxic to the organism that accumulates them and to man. Unfortunately, the information supporting these conclusions is sketchy. Additional information is needed on the uptake, retention, and clearance rates for organotin compounds in:

(i) whole organisms, in which accumulation will be of concern for organisms higher in the food web (to determine if biomagnification occurs, measurements should be made on organisms at various trophic levels);

(ii) reproductive organs, in which accumulation may affect the proliferation of the species; and

(iii) edible tissues, especially muscle and liver, in which accumulation will influence the extent of human consumption.

Mechanisms of Action

In order to understand the actions of organotin compounds on aquatic organisms, to predict their effects, and to regulate them intelligently, it is necessary to establish their actions at the cellular and biochemical levels. It is therefore recommended that the following effects and mechanisms be determined:

(i) effects on blood chemistry and on basic physiological events such as glycogen, lipid and protein metabolism, including effects on enzyme systems to search for biochemical indicator reactions;

(ii) effects on membranes: mitochondrial, chloroplast (e.g. ATPases), and cell membranes;

(iii) biochemical mechanisms of transformations of tin compounds; and

(iv) mechanisms whereby organisms resist organotin compounds or adapt to them.

Effects of Chronic, Sublethal Exposure

Data indicate that trialkyltin compounds are toxic to nontarget marine and freshwater organisms at micromolar concentrations over short periods of time. These data, however, are of little use in establishing environmental hazard levels because nontarget organisms are rarely exposed to such high concentrations of toxicant, but instead may be continuously exposed to low nanomolar concentrations of organotin compounds for prolonged periods of time. It is therefore essential to determine the sublethal effects due to chronic exposure of nontarget organisms to the low concentrations of organotin compounds expected to be encountered in the environment. Of particular concern are effects on reproduction and on growth. Both field studies and controlled ecosystem studies are recommended.

Interactions with Other Stressors

More than 800 toxic chemicals have been identified in the Great Lakes by the International Joint Commission. Additional stresses of concern include low concentrations of dissolved oxygen, and temperature. In any ecosystem aquatic organisms will be exposed to complex combinations of stresses. Essentially nothing is known of the combined effects of organotin compounds and other stresses. Initial research in this area is recommended.

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1.0 INTRODUCTION

Tin as a metal and in organic compounds has a wide variety of uses. In many of its applications, only small amounts of tin are needed to cause the desired effect. This is generally true for the organotin compounds which, during the past 30 years, have developed into important industrial commodities. A further characteristic of tin is that it is unsurpassed by any other metal in the multiplicity of its organic applications. These involve such widely divergent fields as stabilizers for poly(vinyl chloride) (PVC)[α], industrial catalysts, industrial and agricultural biocides, and wood-preserving and antifouling agents, to mention only the most important applications.

The annual world consumption of tin in all forms was about 200 x 10^6 kg in 1976, and of this total about 28 x 10^6 kg was in the form of organotin compounds (Zuckerman et al. 1978). The United States consumed about 11 x 10^6 kg of organotin compounds in that year, and an 11-13% annual growth was predicted for the period 1978-1988. The total annual Canadian market (production and import) for organotin compounds has been estimated to exceed 1 x 10^6 kg.

The increasing annual use of organotin compounds, some of which are very toxic, caused organotin compounds as a class to be placed on Environment Canada's Environmental Contaminants Act Category III list, which essentially meant that further information was required on their occurrence, persistence and toxicity in order to make environmental and human health risk assessments (Environment Canada and Health and Welfare Canada 1979). Since that time, the butyl- and methyltin series of compounds have been found in some Canadian waters and sediments (Maguire et al. 1982; Maguire 1984).

Acting independently of Environment Canada, the Subcommittee on Water of the National Research Council of Canada's Associate Committee on Scientific Criteria for Environmental Quality identified Organotin Compounds in the Aquatic Environment as a priority topic. The result of their concern is this criteria document which examines the critical scientific issues surrounding this topic and describes the fundamental concepts on which criteria are based.

Several aspects of the chemistry and behavior of organotin compounds in the aquatic environment have been the subjects of excellent reviews (e.g. Barnes and Stoner 1959; Ingham et al. 1960; Tobias 1966; Coates et al. 1967; Neumann 1970; Poller 1970; Sawyer 1971; Zuckerman 1976; Zuckerman et al. 1978; Horwitz 1979; Piscator 1979; WHO 1980; Negishi 1980; Davies and Smith 1980, 1982; Duncan 1980; Bock 1981; Bennett 1983; Thayer 1984; Blunden et al. 1984b). This criteria

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[α] A list of abbreviations is given in Appendix I.0.

document, which emphasizes Canadian issues wherever possible, deals with the physical and chemical behavior of organotin compounds in the aquatic environment; the industrial sources of these compounds; analytical methodology for organotin compounds in water, sediment and biota; the environmental persistence and mobility of organotin compounds in aquatic systems; and the effects of organotin toxicants on aquatic organisms. Gaps in knowledge are identified and recommendations are made for research to fill these gaps.

Throughout this document, concentrations are expressed, wherever possible, in units of moles of tin per litre or per kilogram. For biological experiments involving exposure of aquatic organisms to organotin compounds, concentrations are also expressed as a multiple of grams per litre of the appropriate organotin compound. Where the counterion of the organotin compound is not known, the concentration is expressed in the units used by the original authors.

2.0 SOURCES

2.1 INTRODUCTION

The first practical application of an organotin compound, as a mothproofing agent, was not discovered until 1925. Other early industrial applications of organotin compounds included stabilization of chlorinated benzenes and diphenyls used in transformers and capacitors (1932); stabilization of poly(vinyl chloride) by dibutyltin dilaurate and other dibutyltin salts (1936); stabilization of dry spun vinyl-chloride-acetate copolymer fibers (1939); and scavengers for hydrogen chloride released from askarels in certain short-circuited transformers (late 1940's). The biocidal effects of organotin compounds were not studied before the 1950's when such work began at the Institute for Organic Chemistry T.N.O., Utrecht, Holland, under the sponsorship of the International Tin Research Institute in Greenford, Middlesex, England.

Organotin compounds are now one of the most studied organometallic systems in terms of industrial and agricultural applications. This subject has been extensively reviewed in past years (see, for example, Ingham et al. 1960; Zedler and Beiter 1962; Ascher and Nissim 1964; Luijten 1972; Piver 1973; Evans 1974; Bokranz and Plum 1975; Smith and Smith 1975; van der Kerk 1975; Great Lakes Water Quality Board 1976; Lapp 1976; Zuckerman et al. 1978; Thust 1979; Duncan 1980; WHO 1980; Davies and Smith 1982; Bennett 1983). Much of the information in Sections 2.2 and 2.3 has been summarized from these and other reviews. In these sections, the various nonbiocidal and biocidal applications of organotin compounds will be described briefly to provide the foundation for a discussion of Canadian use patterns of these compounds and their routes of entry into the Canadian aquatic environment.

2.2 NONBIOCIDAL APPLICATIONS

2.2.1 STABILIZERS

2.2.1.1 Poly(vinyl chloride)

The largest proportion of organotin compounds produced is used to stabilize poly(vinyl chloride) (PVC) polymers. PVC is used extensively in such areas as food packaging, bottles and the construction industry (flooring, fencing, piping). However, the polymer tends to degrade when heated or when exposed for prolonged periods to ultraviolet light; degradation of only 0.1% causes diminished optical clarity and undesirable coloration (Piver 1973; Evans 1974). The need for stabilization is therefore of particular importance if the PVC requires colorlessness and transparency, e.g. for bottles, films or sheets for food packaging.

The mechanism of PVC degradation (Luijten 1972; Piver 1973; Lapp 1976; Poller 1976; Zuckerman et al. 1978) appears to be related to a dehydrochlorination reaction at an allylic or tertiary chlorine site with the formation of a double bond; the resulting conjugated unsaturated system causes the undesirable characteristics. The mechanism of PVC stabilization by organotin compounds (Hedges 1960; Ingham et al. 1960; Luijten 1972; Piver 1973; Smith and Smith 1975; Poller 1976; Lapp 1976; Parker and Carman 1978; Zuckerman et al. 1978; Mori et al. 1979; Allen et al. 1979; Guyot et al. 1981; Michel 1984) probably involves (i) an exchange of allylic chlorine atoms with the anionic portion of the organotin molecule, inhibiting the onset of the dehydrochlorination reaction; (ii) a reaction with the liberated hydrogen chloride which would otherwise induce further elimination, and production of HX which can add across the unsaturated centers; and (iii) prevention of PVC polymer breakdown, which is initiated by atmospheric oxygen, by antioxidant activity.

About 10% of all PVC produced is stabilized by organotin compounds (Luijten 1972). Diorganotin compounds are effective stabilizers at levels of about 2% (0.5-5%) by weight in the polymer, maintaining both clarity and impact strength (Luijten 1972; Evans 1974). Sulfur-containing mercaptide compounds are particularly useful for heat stabilization (e.g. dibutyltin bis(isooctyl mercaptoacetate); dimethyltin bis(isooctyl mercaptoacetate); dibutyltin bis(lauryl mercaptide); dibutyltin bis(isooctyl thioglycollate)), whereas nonsulfur compounds impart light stability (e.g. dibutyltin dilaurate; bis(tributyltin) oxide; dibutyltin bis(2-ethylhexanoate)). In addition, monoorganotin compounds can be added to diorganotin PVC stabilizers to produce a clearer, more stable PVC (Craig 1980; Anon. 1982; Blunden and Chapman 1982).

2.2.1.2 Other Applications

Organotin stabilizers also prevent the thermal degradation of such chlorinated compounds as transformer oils, rubber paints, paraffins and modified plastics. As well, nonhalogenated compounds (e.g. lubricating oils, cellulose acetate, hydrogen peroxide, polyamides, polyethylene, polypropylene) are stabilized by diorganotin compounds (Hedges 1960; Ingham et al. 1960; Ascher and Nissim 1964; Luijten 1972; Piver 1973).

2.2.2 CATALYSTS

Diorganotin compounds (e.g. dibutyltin diacetate, dibutyltin dilaurate, dibutyltin di(2-ethylhexanoate), dibutyltin dilaurylmercaptide) can be used as catalysts (at 0.3-0.4% levels) in the production of polyurethane foams (Luijten 1972; Piver 1973; Evans 1974; Smith and Smith 1975), enabling the foam to be made directly from hexamethylene diisocyanate and 1,4-butanediol. The compounds catalyze the chain extension reaction so that optimal rates of both chain extension and CO_2 formation reactions can be achieved (Piver 1973).

Diorganotin compounds can also be used as curing catalysts in the room-temperature vulcanization of silicone rubbers used in making dental impressions and encapsulating electronic parts (Piver 1973). The typical catalyst (e.g. dibutyltin dilaurate), added at the 0.1-0.5% level, brings about the cross-linking of silicone at room temperature to form a polymer with elastomeric properties, toughness, flexibility and resistance to temperature, oxidation, ultraviolet radiation and chemicals (Luijten 1972; Piver 1973; Evans 1974; Smith and Smith 1975; Zuckerman et al. 1978).

Use of organotin catalysts leads to the formation of epoxy resins with improved storage properties (Luijten 1972). Both dialkyl- and monoalkyltin compounds can be used as homogeneous catalysts in industrial esterification and transesterification processes (Luijten 1972; Piver 1973; Anon. 1982). Tetrabutyltin compounds can also act as catalysts; when coupled with titanium chloride, they catalyze the low-pressure polymerization of olefins (e.g. ethylene, propylene, vinyl chloride) (Ingham et al. 1960; Luijten 1972).

The mechanism of the catalytic action of organotin compounds has been attributed to the low energy 5d orbitals of the tin atom which can form hexa- and pentacoordinate bonds (Piver 1973).

2.2.3 OTHER USES

Organotin compounds have several additional nonbiocidal industrial applications: (i) to produce strengthening, decorative, or electroconductive layers of tin oxide on glass surfaces (Ingham et al. 1960; Luijten 1972; Evans 1974; Smith and Smith 1975); (ii) as additives (antioxidants) in lubricants and textile oils (Ascher and Nissim 1964; Luijten 1972; Jones 1973); (iii) to render brick, paper, and textiles water-repellent (Luijten 1972; Anon. 1982); (iv) as fireproofing agents for plastics and wool fabrics (Abe et al. 1973; Anon. 1982); (v) in tin-containing polymers and macromolecules, for production of plastic materials of high thermal stability (Luijten 1972); (vi) to enhance the oxidation resistance of aliphatic hydrocarbons (Luijten 1972); and (vii) as dielectric, insulating and cooling agents in electric transformers and capacitors, in synthetic liquids known as askarels (Luijten 1972). The potential for use of some organotin compounds in cancer chemotherapy is currently being investigated (Cardarelli et al. 1983; Bennett 1983; Gielen et al. 1984).

2.3 BIOCIDAL APPLICATIONS

The biocidal uses of organotin compounds were first discovered in the 1950's by a group headed by G.J.M. van der Kerk at the Institute for Organic Chemistry T.N.O. in Utrecht, Holland. Since that time, organotin compounds have found use as fungicides, bactericides and preservatives for wood, textiles, paper, leather and electrical equipment (Piver 1973). The major organotin biocides are bis(tributyltin) oxide, tributyltin fluoride, triphenyltin chloride, triphenyltin hydroxide, and tricyclohexyltin hydroxide.

2.3.1 ANTIFOULING AGENTS

Over 4000 species of microorganisms, plant forms (e.g. diatoms, algae) and animals (e.g. barnacles, mussels, tubeworms, bryozoans, sponges) are capable of adhering to the bottoms of stationary or moving ships and other surfaces immersed in seawater (Evans and Smith 1975; Alzieu et al. 1980). This biofouling may cause serious problems, including: (i) loss of speed; (ii) increased fuel consumption as a result of increased friction due to the roughened surface; (iii) frequent drydocking to replenish antifouling coatings; (iv) increase in buoy and float weight and acceleration of localized corrosion on ship hulls and marine equipment, resulting in high maintenance costs; (v) blockage of seawater conduits and ships' valves; (vi) damage to static offshore structures such as oil and gas platforms, causing design specifications to be exceeded and necessitating increased inspection and maintenance; (vii) fouling in installations using seawater, e.g. for cooling purposes, including desalination and power plants; and (viii) unpredictable distortion in signals from immersed acoustic and electronic navigational devices (Mearns 1973; Phillip 1973; Starbird and Sisson 1973; Evans and Smith 1975; Fischer 1976; Beiter 1976; de la Court 1977; Monaghan et al. 1980; Alzieu et al. 1980; Duncan 1980; Evans 1981; Subramanian and Somasekharan 1981; Dawans 1982). Costs to the international maritime economy as a result of biofouling have been estimated at more than $1 billion per year (Evans and Smith 1975).

A solution to the marine biofouling problem is antifouling paints, which, when applied to submerged surfaces, gradually dissolve in the water, creating a barrier around the surface which is unfavorable to the survival of adhering organisms. The toxic substance commonly contained in these paints is cuprous oxide; however, triorganotin compounds, in particular bis(tributyltin) oxide and tributyltin fluoride, are being used more and more frequently as the active substances in antifouling paints because (i) they provide superior protection over longer periods of time; (ii) they do not promote corrosion; and (iii) they eventually degrade to relatively nontoxic compounds in the aqueous environment (Hoffman et al. 1978). The use of these trialkyltin derivatives is not restricted to wooden hulls but extends to marine vessels constructed of aluminum and other metals with no problems resulting from corrosion (Smith and Smith 1975).

The effectiveness of the antifouling barrier created by the paint is maintained only as long as levels of the active agent exceed the repellancy threshold for most resistant organisms. The leaching rate, or the amount of active substance released per day by a given painted area, is therefore an extremely important parameter. A large number of commercial and experimental paint formulations have been developed to maximize antifouling protection by reducing the leaching rate and hence extending the active lifetime of the agent. The characteristics of these antifouling formulations, including chemical structure (e.g. type of organotin compound, binder, matrix, solvent), release rate, and effectiveness, have been discussed in detail by many researchers (see, for example, Bennett and Zedler 1966; Woodford 1972; Phillip 1973; Beiter 1976; de la Court 1977; de la Court and de Vries 1977; Monaghan et al. 1978a, b, 1980; Subramanian and Somasekharan 1981; Evans 1981; Hsu 1982; Dawans 1982; Battais et al. 1982). In general, the formulation may consist of (i) a conventional paint system; (ii) an elastomeric system in which the organotin compound is incorporated into, for example, a chloroprene rubber; or (iii) a polymeric system in which the trialkyltin acrylate or methacrylate is copolymerized with, for example, vinyl chloride (Evans and Smith 1975; Alzieu et al. 1980). Triorganotin compounds are generally found at concentrations of 2-10% in antifouling paints.

2.3.2 FUNGICIDES AND BACTERICIDES

The fungicidal properties of organotin compounds were first discovered in the 1950's by van der Kerk and Luijten (1954). Since that time, organotin compounds have been used extensively in agriculture and industry because of their fungicidal and bactericidal properties (Kaars Sijpesteijn et al. 1969; Luijten 1972; Gitlitz 1976; Srivastava et al. 1977; Davies and Smith 1982).

The use of triorganotin compounds as agricultural fungicides is limited by their phytotoxicity; only the phenyl and cyclohexyl derivatives are sufficiently nonphytotoxic to be useful (Luijten 1972; Kumpulainen and Koivistoinen 1977). Triphenyltin hydroxide and triphenyltin acetate are used against such fungi as potato blight and leaf spot of sugar beet and celery, as well as fungi affecting celeriac, leek, carrots, hops, onions and rice, and causing tropical plant diseases in ground nuts, pecans, coffee and cocoa (Ryan et al. 1972; Luijten 1972; Smith and Smith 1975; Kumpulainen and Koivistoinen 1977; Soteros 1979; Duncan 1980).

Another major use of triorganotin compounds is as a wood preservative, against such wood-destroying fungi as *Poria monticola*, *Coniophora olivacea*, and *Fomes lividus*, as well as against wood-boring insects (e.g. furniture beetle) (Ingham et al. 1960; Hedges 1960; Zedler and Beiter 1962; Vind and Hochman 1962b; Ascher and Nissim 1964; Luijten 1972; Da Costa and Osborne 1972; Jensen 1977; Craig 1980; Blunden and Chapman 1982). A 0.1% solution of trialkyltin preservatives is sufficient to protect wood against wood-destroying fungi; higher concentrations are required to protect wood from attack by insects (Luijten 1972). The three trialkyltin compounds in current use as fungicides are bis(tributyltin) oxide, tributyltin naphthenate and tris(tributylstannyl) phosphate. Richardson (1970) suggested that bis(tributyltin) oxide protected wood cellulose against attack by brown rot fungus by chemically blocking the vulnerable hydroxyl groups in the cellulose chains, while it acted as a simple toxicant towards wood-boring insects. Later work indicated that the organotin compound reacts with carbon dioxide in the wood to form bis(tributyltin) carbonate (Smith et al. 1977; Hill 1984).

Other important fungicidal and bactericidal applications of triorganotin compounds include: (i) conferring resistance to fungal attack on paints, ropes, leather, fabrics, canvas, concrete and mortar; (ii) eliminating slime formation in the paper production industry, in industrial cooling water, and in water used for the secondary recovery of oil; (iii) disinfecting hospitals (often in conjunction with formol and quaternary ammonium compounds) against staphylococcal contamination through use on clothing, bed linen, surgical masks, floors, walls, etc.; and (iv) controlling the development of microorganisms in underground gas reservoirs (Ingham et al. 1960; Hedges 1960; Zedler and Beiter 1962; Ascher and Nissim 1964; Luijten 1972; Steele and Drisko 1976; Kumpulainen and Koivistoinen 1977; Thust 1979; O'Neill and Drisko 1980).

2.3.3 INSECT AND MITE CONTROL

Triorganotin compounds have found much use as insecticides against such domestic pests as houseflies, cockroaches and mosquito larvae, as well as against such agricultural pests as cotton bollworm and tobacco budworm (Luijten 1972). In addition to these toxic effects, triorganotin compounds also exert antifeeding effects (Ascher 1979) against, for example, the potato tuber moth and the striped maize borer (Meisner and Ascher 1965), gypsy moth larvae (Meisner and Skatulla 1975), caterpillars (Duncan 1980) and cotton leafworm (Abo-Elghar and Radwan 1971). They also act as chemosterilants, interfering with insect reproduction (Luijten 1972; Kenaga 1975).

Several triorganotin compounds are well known for their acaricidal activity (Knowles 1976). Tricyclohexyltin hydroxide, for example, is used to control mites on apple and pear trees, stone fruits, strawberries, citrus, grapes and other crops (Smith and Smith 1975; Kumpulainen and Koivistoinen 1977; Schuster et al. 1979; Duncan 1980).

2.3.4 ANTHELMINTICS

Dialkyltin compounds, in particular dibutyltin dilaurate and dibutyltin maleate, are very effective agents for the control of helminthic and protozoal infections (e.g. cestodes, tapeworms, nematodes, roundworms) in poultry (Kerr 1952; Ingham *et al.* 1960; Luijten 1972). In general, these compounds are more active toward cestodes than toward nematodes. Dialkyltin compounds are also used to control other parasitic diseases in poultry, sheep and swine (Luijten 1972).

2.3.5 MOLLUSCICIDES

Triorganotin compounds, in particular bis(tributyltin) oxide and tributyltin fluoride, may be used extensively in the future in tropical countries to combat the disease bilharziasis or schistosomiasis. This disease is transmitted by worms of the genus *Schistosoma* which use several snail species as their intermediate hosts (de Villiers 1965); the effect of the organotin compound is on the snail vector, not the parasitic worms. The triorganotin compounds, which have been used in limited field trials, are most effective in formulations which feature a continuous release (by a diffusion/dissolution mechanism) of the toxicant which is soluble in an elastomeric matrix (e.g. natural rubber or ethylene-propylene rubber) (Cardarelli 1974; Shiff and Evans 1977; Allen *et al.* 1980; Cardarelli and Evans 1980).

2.4 USE PATTERNS

Zuckerman *et al.* (1978) estimated the annual world consumption of tin to be $\approx 180 \times 10^6$ kg in 1976; of this, $\approx 25 \times 10^6$ kg was in the form of organotin compounds. Davies and Smith (1982) estimated that the use of organotin compounds in industry had risen to ($\approx$30-35) x 10^6 kg in 1980 from $\approx 5 \times 10^6$ kg worldwide in 1965. Of current production, about two-thirds is used for stabilization of PVC plastics and 8.5% for biocides (Craig 1980).

The subject of Canadian use patterns has been well discussed in two Environment Canada documents, by MARTEC Ltd. (1979) and Jones and Millson (1982). Much of the information in the following sections has been summarized from these reports.

It has been estimated that the total annual Canadian market (production and import) for organotin compounds exceeds 1×10^6 kg (Jones and Millson 1982). This can be compared with an estimate of $\approx 11 \times 10^6$ kg consumed annually in the United States (Zuckerman *et al.* 1978).

In Canada, about 10 organotin compounds are consumed in large amounts (Table 2-1). Of these, only dibutyltin dilaurate and stannous 2-ethylhexanoate, which is not a true organotin compound, are

Table 2-1. Organotin compounds used in Canada (from Jones and Millson 1982).

Compound	Uses
Dibutyltin bis-(isooctyl mercaptoacetate)	Stabilizer for PVC used in siding, eavestroughs, and soffits
Dibutyltin dilaurylmercaptide	Polyurethane foam catalyst; feed additive
Stannous 2-ethylhexanoate[α,β]	Polyurethane foam catalyst
Dibutyltin oxide	Precursor for dibutyltin dilaurate
Dibutyltin dilaurate[β]	Chicken feed additive; catalyst for urethanes; esterification catalyst
Bis(tributyltin) oxide	Slimicide in cooling water towers; antifouling additive for marine paint; wood preservative
Tributyltin fluoride	Antifouling additive for marine paint
Dioctyltin maleate	Stabilizer for rigid PVC pipe for potable water supplies
Dibutyltin diacetate	Catalyst for flexible foams
Dioctyltin bis-(isooctyl mercaptoacetate)	Stabilizer for plastics used in food packaging

[α] Not a true organotin compound, but rather a tin salt.

[β] Manufactured in Canada.

manufactured in Canada (MARTEC Ltd. 1979); these constitute less than 10% of the organotin compounds used in Canada. The remainder is presumably imported. In 1976, for example, approximately 4100 kg of bis(tributyltin) oxide were imported, primarily from U.S. manufacturers; in 1977, 1300 kg were imported (MARTEC Ltd. 1979). Importers of organotin compounds used in Canada are listed in Table 2-2. None of the organotin compounds produced in Canada is exported.

Accurate figures for the quantities of organotin compounds marketed in Canada are not easily obtained, although some estimates have been published in the MARTEC Ltd. (1979) report. U.S. data are more readily available. Estimates of annual U.S. production of selected alkyltin compounds between 1965 and 1986 are shown in Table 2-3 by use area and in Table 2-4 by compound. Quantities of organotin compounds imported by the United States between 1966 and 1974 are shown in Table 2-5. Exports over this time period averaged about 4-5% of total annual production (Lapp 1976).

The Canadian market in organotin compounds is dominated by dibutyltin bis(isooctyl mercaptoacetate), sold by M & T Chemicals (which accounted for 90% of Canadian sales of organotin compounds in 1977) as Thermolite 31. This compound accounts for more than 75% by weight of consumption; it is utilized in the manufacture of rigid and semi-rigid PVC products which are used extensively in the construction industry. According to Jones and Millson (1982), the major end uses for organotin compounds in Canada are as PVC stabilizers (80-82%), catalysts (16-17%), and biocides (2-3%).

A similar situation exists in the United States. Dibutyltin bis(isooctyl mercaptoacetate) dominates the market, constituting 33 x 10^6 of the 51 x 10^6 kg of alkyltin compounds produced between 1965 and 1974. This is because the major area of utilization (80% of total annual production) is as a heat stabilizer for rigid and semi-rigid PVC. Dioctyltin compounds are used only in PVC in contact with food; dibutyltin dilaurate is used as a catalyst in foam and elastomer production and as a poultry anthelmintic; and bis(tributyltin) oxide and tributyltin fluoride are used as biocides.

In Canada, as of May 1984, 18 companies had registered, under the Pest Control Products (PCP) Act, a total of 48 commercial and domestic products that contain organotin compounds as the guaranteed ingredient (Agriculture Canada 1984). Two triorganotin compounds were registered under the PCP Act through May 1984 for crop protection in Canada: tricyclohexyltin hydroxide (Plictran, cyhexatin); and di(tri-(2-methyl-2-phenylpropyl)tin) oxide (Vendex, fenbutatin oxide, hexakis (β,β-dimethylphenethyl) stannoxane). Plictran is widely utilized to protect crops, primarily apples, pears, peaches and nectarines. Vendex is a miticide for use on ornamentals in the field and in the greenhouse.

Table 2-2. Producers and importers of organotin compounds in Canada in 1977 (from Millson and Jones 1980).

Company	Compound
Producers	
M & T Chemicals (Hamilton)	Stannous 2-ethylhexanoate Dibutyltin dilaurate
Importers	
M & T Chemicals (Hamilton)	Dimethyl-, dibutyl-, tributyltin esters and salts
Cincinnati Milacron Canada Ltd. (Toronto)	Dibutyl- and tributyltin esters and salts
Nuodex (Toronto)	Maleate and mercaptide tin stabilizers
Albert Chemicals Ltd. (Willowdale)	-
Chemroy (Downsview)	Dibutyltin esters and salts
Dearborn Chemical Co. (Mississauga)	Bis(tributyltin) oxide
Kingsley & Keith (Montreal)	Tributyltin esters and salts
International Chemicals Canada (Mississauga)	Dibutyl- and tributyltin esters and salts
Cardinal Chemical (U.S.A.)	Maleate and mercaptide tin stabilizers

Table 2-3. Estimated annual U.S. consumption of selected alkyltin compounds by use area (after Zuckerman *et al*. 1978)[a].

	Annual consumption (10^6 kg)					
Year	PVC heat stabilizers	Catalysts	Biocides	Anthelmintics	Miscellaneous excluding exports	Total
1965	1.6	0.23	0.23	0.068	0.16	2.3
1966	2.6	0.32	0.27	0.073	0.15	3.4
1967	2.9	0.45	0.32	0.077	0.23	4.0
1968	3.5	0.64	0.36	0.082	0.24	4.8
1969	4.0	0.82	0.41	0.086	0.27	5.6
1970	5.0	1.0	0.50	0.095	0.26	6.9
1971	5.4	1.2	0.59	0.10	0.30	7.6
1972	7.1	1.4	0.68	0.10	0.073	9.4
1973	7.8	1.7	0.77	0.11	0.12	10.5
1974	7.4	2.0	0.91	0.11	0.086	10.5
1975	6.0	1.7	0.68	0.091	0.091	8.6
1976	7.3	2.3	0.91	0.12	0.091	10.7
1981	10-12	3.4	2.3	0.16	0.27	16.1-18.1
1986	13-15	4.5	4.5	0.23	0.45	22.7-24.7
Total (1965-1976)	61	14	6.6	1.1	2.1	84

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[a] The original sources of data are Lapp (1976) and U.S. EPA (1977).

Table 2-4. Estimated annual U.S. production of selected alkyltin compounds (after Zuckerman *et al.* 1978)[α].

Year	Production (10^6 kg.a^{-1})[β]											
	Bu IOMA	Me IOMA	Bu LM	Bu Maleate	Oct. IOMA	Oct. Maleate	Mixed metals	DBTDL	DBTH	TBTO	TBTF	Total
1965	1.0	-	0.45	0.10	-	-	-	0.27	-	0.39	-	2.2
1966	2.1	-	0.45	0.10	-	-	-	0.41	-	0.42	-	3.5
1967	2.2	-	0.41	0.22	-	-	-	0.55	-	0.54	-	3.9
1968	2.8	-	0.41	0.24	0.073	0.0091	-	0.73	-	0.60	-	4.9
1969	3.2	-	0.41	0.26	0.091	0.014	-	0.91	-	0.68	-	5.6
1970	3.8	0.30	0.50	0.27	0.15	0.023	-	1.1	-	0.76	0.0045	6.9
1971	3.7	0.64	0.50	0.28	0.17	0.027	-	1.3	-	0.90	0.0091	7.5
1972	4.8	1.3	0.59	0.12	0.25	0.036	-	1.1	0.36	0.73	0.023	9.3
1973	4.6	1.8	0.59	0.10	0.28	0.036	0.36	1.4	0.41	0.50	0.036	10.1
1974	4.2	2.0	0.59	0.095	0.17	0.032	0.23	1.6	0.50	0.94	0.055	10.4
1975	3.2	1.8	0.45	0.091	0.23	0.032	0.18	1.4	0.41	0.64	0.14	8.6
1976	4.1	2.0	0.50	0.10	0.27	0.032	0.23	2.0	0.45	1.0	0.23	10.9
1981	5.9-6.6	3.0-3.6	0.91	0.15	0.41	0.091	0.0	2.7	0.86	2.1	0.45	16.6-17.9
1986	6.8-8.4	3.6-4.5	1.4	0.20	0.55	0.14	0.0	3.6	1.1	4.1	0.91	22.4-24.9
Total (1965-1976)	40	9.8	5.9	2.0	1.7	0.24	1.0	13	2.1	8.1	0.50	84

[α] Original data are from Lapp (1976) and U.S. EPA (1977).

[β] Bu IOMA = Butyltin isooctyl mercaptoacetate plus blends
Me IOMA = Methyltin isooctyl mercaptoacetate plus blends
Bu LM = Dibutyltin bis(laurylmercaptide)
Bu Maleate = Dibutyltin alkylmaleate esters
Oct. IOMA = Dioctyltin-S,S'-bis(isooctyl mercaptoacetate)
Oct. Maleate = Dioctyltin maleate polymers
DBTDL = Dibutyltin dilaurate
DBTH = Dibutyltin bis(2-ethylhexanoate)
TBTO = Bis(tributyltin) oxide
TBTF = Tributyltin fluoride

Table 2-5. Quantities of alkyltin compounds imported by the United States, 1966-1974 (after Lapp 1976)[α].

Compound	Quantity imported (kg)			
	1966	1972	1973	1974
Dibutyltin dichloride	-	-	-	1 565
Dibutyltin oxide	156 627	327 179	112 886	32 455
Dioctyltin oxide	-	5 908	38 620	21 673
Bis(tributyltin) oxide	507	25 617	4 470	37 616
Tributyltin fluoride	-	4 155	2 245	-
Tributyltin chloride	-	1 055	1 318	-
Tetrabutyltin	-	11 364	-	65 468
Total	157 134	375 278	159 539	158 777

[α] Data from weekly listing in Chemical Marketing Reporter.

The use of triphenyltin hydroxide (Du-Ter, fentin hydroxide) as a fungicide on potatoes was discontinued in 1980.

Five other organotin compounds used in products registered under the PCP Act are bis(tributyltin) oxide, tributyltin chloride, tributyltin maleate, tributyltin neodecanoate, and tributyltin methacrylate (Agriculture Canada 1984). These are employed as fungicides for wood and wood products, slimicides for industrial water, germicides for fabrics, leather, and paints, disinfectants for hospitals and farm equipment, etc.

This section has thus far discussed past and present trends in consumption of organotin compounds in Canada and the United States. Future use patterns for the United States were predicted by Lapp (1976) as follows: increased consumption with yearly fluctuations depending on the poly(vinyl chloride) market; no increase in the catalyst market; and good growth in the area of biocidal applications.

2.5 ROUTES OF ENTRY INTO THE ENVIRONMENT

The fluxes of organotin compounds into the aquatic environment are in general through direct input routes via air or water as a result of production, processing, use or disposal, and indirectly through biotic and abiotic transformations.

2.5.1 PRODUCTION AND PROCESSING

Very little, if any, information exists concerning the amounts of organotin compounds entering the Canadian environment by the production and processing routes. Only one manufacturing location for organotin compounds is known to exist in Canada; it converts dibutyltin oxide to dibutyltin dilaurate. Information on losses to the environment during production is unavailable; the wastes are treated chemically before disposal. Facilities producing polyurethane or PVC resins stabilized with organotin compounds may release them into air, water or solid industrial wastes. Again, it is not known what quantities of organotin compounds enter the environment by this route (Jones and Millson 1982).

In the United States, it has been estimated that 0.5% of production (0.054×10^6 kg) is lost to the environment by disposal routes at the manufacturing source. Industrial disposal options include evaporation, bacterial degradation settling ponds, sludge burial, deep-well injection, hydrolysis and precipitation methods, discharge to municipal treatment plants, recovery and recycling techniques, etc. (Zuckerman et al. 1978). Disposal methods, losses and reclamation processes for U.S. companies producing organotin compounds have been described by Lapp (1976).

2.5.2 PRODUCT USE

Although the major use of organotin compounds in Canada is in the area of heat stabilization, the greatest potential for direct contact with the environment probably results from biocidal applications (Lapp 1976). Organotin compounds used in biocidal paints and preservatives, for example, may leach into water during their use, particularly in the vicinity of docks and marinas. About 600 L of pure bis(tributyltin) oxide is used annually in the Maritimes as a preservative on lobster pots (Millson and Jones 1980); the amount of bis(tributyltin) oxide that escapes to the environment during the use, storage and treatment of these pots is not known. The occurrence of high concentrations of butyltin species in harbors (Maguire et al. 1982; Maguire 1984) has been attributed to the use of tributyltin compounds in antifouling paints.

Lapp (1976) calculated the quantities of organotin compounds released to the environment by antifouling coatings on U.S. marine craft (Table 2-6) assuming a 3-year lifetime for an antifoulant coating. At an average loss rate of 30% for the first year and 25% for the next 2 years, it can be estimated that in 1975, for example, the total quantity of trialkyltin compounds released to seawater was 59 090 kg from 1973 and 1974 plus 30% of the total quantity applied in 1975. Note that an unknown amount of trialkyltin compounds would also leach from boats and ships of foreign registry. Waste grit would contain 18 180 kg resulting from the removal of coatings applied in 1973. Lapp (1976) suggested that the method of disposal of sandblast grit was probably deposition in water adjacent to the shipyard. Alternatively, the wastewater could be discharged to a local municipal wastewater treatment facility (Argaman et al. 1984).

Organotin compounds used in crop protection in Canada may also enter the environment during use. Although Plictran is applied in orchards by ground equipment, not by aircraft, it can volatilize from moist surfaces by co-distillation with water (Smith et al. 1976). The extent to which this occurs is not known, although it has been suggested that this is not a significant route of entry because of the limited acreage treated and the high air dilution factor (Jones and Millson 1982). Increased organic tin concentrations in apple orchard soil have been found following application of tricyclohexyltin hydroxide to the orchards, but no organic tin was detected in river water near the orchards (Jin et al. 1982).

2.5.3 PRODUCT DISPOSAL

The industrial and consumer disposal of organotin compounds which have been used as stabilizers, catalysts, biocides and preservatives may also result in environmental exposure. In Canada,

Table 2-6. Quantities of trialkytin compounds released to seawater from marine antifouling paints in the United States, 1965-1974 (after Lapp 1976).

Year	Approximate total quantity used (10^3 kg)	Quantity released to seawater (10^3 kg)	Quantity in residual grit (10^3 kg)
1965	45.5	13.6+	-
1966	45.5	25.0+	-
1967	34.1	33.0	9.1
1968	40.9	32.2	9.1
1969	63.6	37.8	6.8
1970	68.6	46.7	8.2
1971	65.0	52.6	12.7
1972	68.2	53.9	13.7
1973	90.9	60.6	13.0
1974	145.5	83.4	13.6

disposal methods usually consist of sanitary landfill or incineration. Little is known about the rates at which organotin additives leach from plastic matrices in landfills, although several researchers have found that soil has such a high affinity for organotin compounds that leaching from a landfill and subsequent pollution of groundwater are highly improbable (Barnes et al. 1973; Slesinger 1977; Harris et al. 1979). On the other hand, tin associated with soil can be mobilized by earthworms (Gile et al. 1982). With respect to disposal of spent blast cleaning abrasives containing organotin paint particles (10-50 $mg.kg^{-1}$ in various blast waste samples; Slesinger 1977), Ticker et al. (1977) found that their fluidized bed incineration oxidized all organic matter in the abrasives, rendering it harmless.

In the United States, landfill and incineration are used to dispose of an estimated 2.3×10^6 kg of organotin compounds in PVC annually, whereas approximately 0.45×10^6 kg of organotin compounds in biocides are released each year to the environment via municipal sewers, surface waterways, harbors and oceans (U.S. EPA 1977) (Table 2-7).

2.5.4 OTHERS

There are other, less direct, routes of entry of organotin compounds into the aquatic environment. Methyltin species, for example, have been found in precipitation (e.g. Braman and Tompkins 1979; Tugrul et al. 1983), and atmospheric transport could explain the presence of methyltin species in areas remote from industrial activity (Maguire et al. 1982).

Another possible source of organotin compounds is the methylation of inorganic tin. This process will be discussed in detail in Section 5.4.2.

Table 2-7. Estimated quantities of organotin compounds released to the environment in 1976 by various routes (after Zuckerman *et al*. 1978)[α].

Product containing organotin compound	Content of organotin compound (10^6 kg)	In use (10^6 kg)	Discarded (10^6 kg)	Environmental quantity (10^6 kg)	Environmental route
Plastics, PVC, polyurethane, silicones	9.5	7.3	2.3	0.23 2.0	Incineration, landfill
Antifouling paints	0.36	0.18	0.18	0.18	Ocean and estuarine water, sediments
Industrial and consumer slimicides and other biocides	0.32	0.23	0.091	0.091	Rivers and estuaries, sediments
Latex paints	0.23	0.22	0.011	0.00011	Dumped or leaked
All other applications including export	0.50	0.57	0.15	0.15	Landfill

[α] Original source of data is U.S. EPA (1977).

3.0 CHEMISTRY

3.1 INTRODUCTION

For the purposes of this document, an organotin compound is defined as one containing a tin-to-carbon bond. A brief outline of the chemistry of these compounds follows, with emphasis on reactions and properties of environmental and analytical significance. Synthetic routes to compounds used commercially are also delineated. Tables of properties of selected organotin compounds are given in Appendix III.0.

Throughout this document, the formula R_nSnX_{4-n} (n = 1-4; R = alkyl or aryl; X = H, OR', halogen, etc.) is used to symbolize known compounds. The symbol Q, as in R_nSnQ_{4-n}, is used in those cases where only R is known.

The first organotin compound to be isolated was diethyltin diiodide, prepared by Frankland (1849) by the "direct synthesis" method in vogue at that time (eq. 3-1).

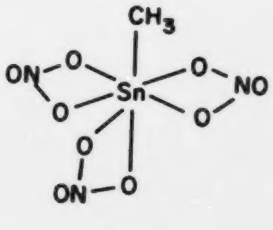
$$2C_2H_5I + Sn \longrightarrow (C_2H_5)_2SnI_2 \qquad (3\text{-}1)$$

Essentially the same procedure is now used industrially for the manufacture of dimethyltin dichloride (Lapp 1976). The discovery that Grignard reagents RMgX (also "direct synthesis" products) readily react with $SnCl_4$ to afford R_4Sn (eq. 3-2) opened the way to the preparation of a large number of derivatives, especially after the discovery of the Kocheshkov (1926) conproportionation reaction (redistribution reaction; Moedritzer 1971) (eq. 3-3).

$$4RMgX + SnCl_4 \longrightarrow R_4Sn + 4MgXCl \qquad (3\text{-}2)$$

$$3R_4Sn + 3SnCl_4 \rightleftharpoons 2R_3SnCl + 2R_2SnCl_2 + 2RSnCl_3 \qquad (3\text{-}3)$$

Like that of carbon, organotin chemistry is dominated by the valence of four, although, unlike carbon, the coordination number around tin can be greater (up to seven as in the ester $CH_3Sn(NO_3)_3$ (1); Brownlee et al. 1971) because of the presence of easily accessible vacant d-orbitals. Although no further mention of them will be made in this chapter, it is worth noting that stable two- and three-coordinate organotin compounds are known (e.g. 2; Almenningen et al. 1967; Goldberg et al. 1976).



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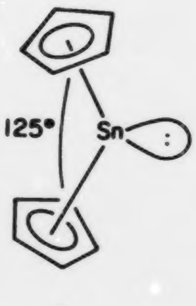
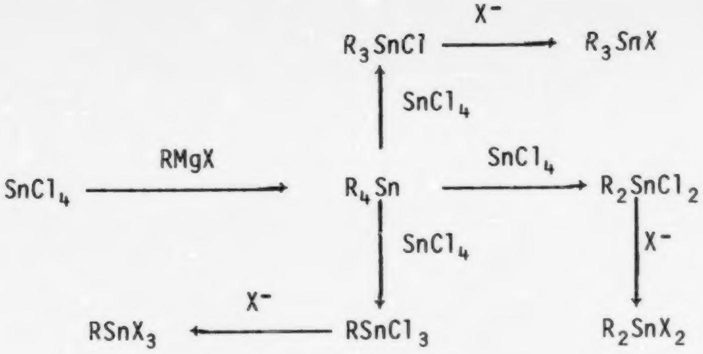


2

Most of the organotin chemistry treated in this survey is outlined in Scheme 1.

Scheme 1



where R = alkyl or aryl
$X = H, OR^1, OCOR^1, NR^1_2$, etc.

All three classes, R_3SnX, R_2SnX_2 and $RSnX_3$, have commercial uses (see Chapter 2 and Appendix III.0), with production being about 3.5×10^6 $kg.a^{-1}$ (Davies and Smith 1982).

The most recent general accounts of organotin chemistry are available in Davies and Smith (1980, 1982). A slightly older summary was written by Bloodworth (1972). Books by Neumann (1970), Poller (1970) and Sawyer (1971-1972) give more complete coverage of the literature to 1970. The Gmelin Handbuch der Anorganischen Chemie (Schumann and Schumann 1975-1979) contains information on a large number of organotin compounds belonging to the classes R_4Sn, R_3R^1Sn, $R_2R^1{}_2Sn$, $R_2R^1R^2Sn$, $RR^1R^2R^3Sn$, organotin fluorides, chlorides, and hydrides[α]. Zuckerman et al.(1978) have written an account of organotin compounds in biology and the environment, and Brinckman (1981) has provided an account of some biological aspects of organotin compounds.

3.2 SYNTHESIS OF R_4Sn COMPOUNDS

The most important route to these compounds involves the reaction of a tin(IV) compound, usually $SnCl_4$, with an organometallic species such as a Grignard or organoaluminum reagent (eqs. 3-2, 3-4).

$$4R_3Al + 3SnCl_4 \longrightarrow 3R_4Sn + 4AlCl_3 \qquad (3\text{-}4)$$

[α] Additional volumes on organotin bromides, iodides, pseudohalides and sulfur compounds are now available.

The alkylaluminum compounds are readily available industrially and the reactions can be carried out conveniently in high yield in the absence of solvent. The Grignard reactions also give high yields, especially if the minimum amount of stabilizing solvent (usually an ether) is used together with a higher boiling inert solvent. It is possible to stop some of these reactions before complete substitution to give pure products, especially if R is bulky, as in the synthesis of tricyclohexyltin chloride (see Scheme 2, Section 3.3.1; Gitlitz 1976).

The use of organometallic species is important in the synthesis of mixed compounds, such as is shown in eq. 3-5. Such mixed compounds have analytical applications (Maguire et al. 1982; Chau et al. 1982).

$$(CH_3)_3SnCl + RLi \longrightarrow (CH_3)_3SnR + LiCl \qquad (3\text{-}5)$$

Examples of other less important routes are given in eqs. 3-6 to 3-8.

$$(n\text{-}C_4H_9)_2SnCl_2 + 2(n\text{-}C_4H_9)Cl \xrightarrow{Na} (n\text{-}C_4H_9)_4Sn + 4NaCl \qquad (3\text{-}6)$$

The R_4Sn compound in this case (Wurtz coupling) can be converted back to R_2SnCl_2 via the redistribution reaction (eq. 3-3 and Section 3.3.1) with $SnCl_4$ (van der Kerk and Luijten 1957).

$$(C_2H_5)_3SnH + CH_2{=}CHCOOCH_3 \longrightarrow (C_2H_5)_3SnCH_2CH_2COOCH_3 \qquad (3\text{-}7)$$

(Hydrostannation; Neumann et al. 1962)

$$(CH_3)_3SnLi + C_2H_5Br \longrightarrow (CH_3)_3SnC_2H_5 + LiBr \qquad (3\text{-}8)$$

(Stannyl metallic reagents; Cardin et al. 1968)

3.3 CLEAVAGE OF TIN-CARBON BONDS

3.3.1 REDISTRIBUTION REACTION

The most important cleavage reaction from the industrial point of view is the redistribution reaction shown in eq. 3-3 (Section 3.1). Here alkyl- or aryltin substituents are changing sites with halogen-tin substituents in reactions that eventually reach an equilibrium state if left long enough. It can be seen that 4+1 = 5 compounds are in the equilibrium mixture which can be defined by the set of 4-1 = 3 equilibria (eq. 3-9).

$$2SnR_yX_{4-y} \overset{K_y}{\rightleftharpoons} SnR_{y-1}X_{4-y+1} + SnR_{y+1}X_{4-y-1} \qquad (3\text{-}9)$$

where $K_y = [SnR_{y-1}X_{4-y+1}][SnR_{y+1}X_{4-y-1}]/[SnR_yX_{4-y}]^2$ and $y = 1, 2$ or 3.

In the case of an ideal random mix, simple statistics give $K_1 = 0.375$, $K_2 = 0.444$, and $K_3 = 0.375$. Deviations from these values are an indication of the nonadditivity of bond energies resulting in a non-zero value of ΔH° for the reaction. Departures are greater when R and X are chemically dissimilar, as in the most frequently encountered case, R = alkyl(aryl) and X = halogen, when formation of the mixed species is favored.

Generally, if the compound SnR_yX_{4-y} is desired in maximum yield, the ingredients SnR_4 and SnX_4 need to be combined in the ratio $y/(4-y)$ in a single-phase reaction. However, higher yields can be obtained by disturbing the equilibrium by, for example, removal of a component by distillation.

The first step in these reactions seems to be as in eq. 3-10, so temperature (kinetic) control can also be used to increase the yield of the desired species.

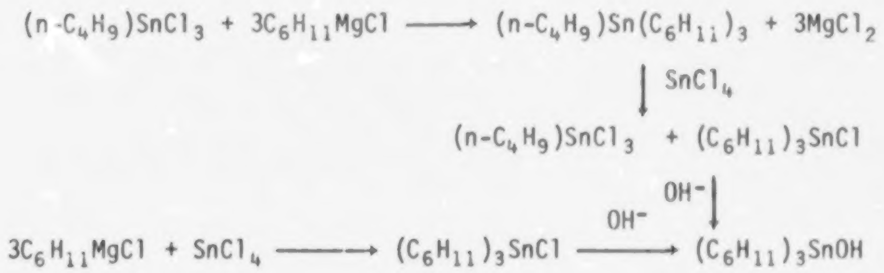
$$R_4Sn + SnCl_4 \longrightarrow RSnCl_3 + R_3SnCl \qquad (3\text{-}10)$$

Complex formation is also of use as in the $(CH_3)_4Sn/SnCl_4$ reaction in DMSO where the adduct $(CH_3)_3SnCl.DMSO$ is insoluble.

The rates of redistribution decrease in the order Cl > Br > I.

Not unexpectedly, mixed tetraorganotin compounds also undergo this reaction, as in the synthesis of the important pesticide tricyclohexyltin hydroxide shown in Scheme 2 (Gitlitz 1976).

Scheme 2


$(n\text{-}C_4H_9)SnCl_3 + 3C_6H_{11}MgCl \longrightarrow (n\text{-}C_4H_9)Sn(C_6H_{11})_3 + 3MgCl_2$
$SnCl_4$
$(n\text{-}C_4H_9)SnCl_3 + (C_6H_{11})_3SnCl$
OH^-
OH^-
$3C_6H_{11}MgCl + SnCl_4 \longrightarrow (C_6H_{11})_3SnCl \longrightarrow (C_6H_{11})_3SnOH$

3.3.2 HALOGEN CLEAVAGE

This is a convenient route to the preparation of mono- and dihalo derivatives (eq. 3-11).

$$R_4Sn + X_2 \xrightarrow{solvent} R_3SnX + RX \qquad (3\text{-}11)$$

where X = Cl, Br; solvent = CCl_4, etc.

In the case of the unsymmetrical derivatives, R^1R_3Sn, the ease of cleavage from tin is in the order $C_6H_5 > C_6H_5CH_2 >$ vinyl > alkyl. Less bulky alkyl groups are cleaved more easily, as illustrated in eq. 3-12 (Boue et al. 1968; Davies and Smith 1982).

$$(CH_3)_3SnC_6H_{11} \xrightarrow{Br_2} (CH_3)_2(C_6H_{11})SnBr + CH_3Br \qquad (3\text{-}12)$$

In the case of vinyl groups, the configuration at the double bond is retained on halogen cleavage.

3.3.3 CLEAVAGE BY PROTIC ACIDS

An example of cleavage by protic acids is given below (eq. 3-13) (Henderson and Holliday 1965). Anhydrous acids are usually employed.

$$(C_6H_5)_4Sn + RCO_2H \longrightarrow (C_6H_5)_3SnOOCR + C_6H_6 \qquad (3\text{-}13)$$

3.3.4 CLEAVAGE BY INORGANIC HALIDES

A number of inorganic halides, including $HgCl_2$, BCl_3, $AlCl_3$, $SiCl_4$, $SbCl_3$, and PF_6, cleave Sn-C bonds, as in the following example, which is of synthetic utility when R = C_6H_5 (Seyferth et al. 1967) and which may be of environmental significance when R = CH_3 since methylmercury species are produced (Brinckman 1981; Chau 1983) (eq. 3-14).

$$R_4Sn + HgCl_2 \longrightarrow R_3SnCl + RHgCl \qquad (3\text{-}14)$$

3.3.5 CLEAVAGE BY ORGANOLITHIUM REAGENTS

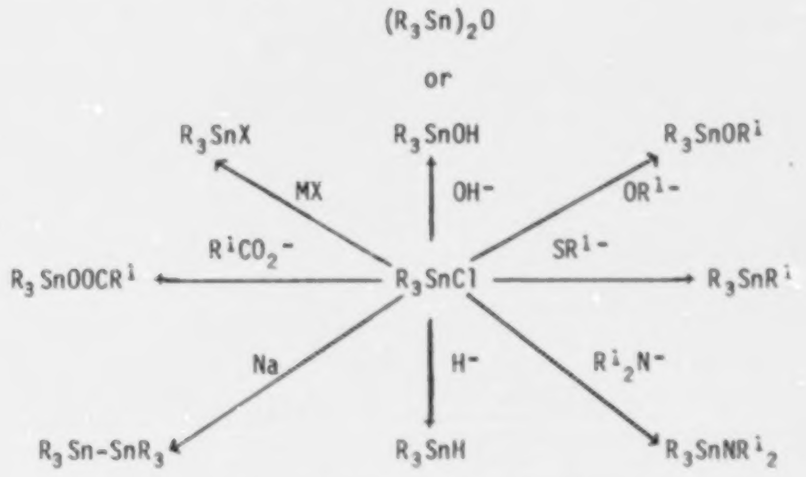
Although these reactions are not important in an environmental context, they do have synthetic importance (e.g. eq. 3-15) (Seyferth and Weiner 1961; Davies and Smith 1982).

$$(CH_2{=}CH)_4Sn + 4C_6H_5Li \longrightarrow 4CH_2{=}CHLi + (C_6H_5)_4Sn \qquad (3\text{-}15)$$

3.4 COMPOUNDS WITH TIN-HALOGEN OR TIN-PSEUDOHALOGEN BONDS

The halogen derivatives are the key intermediates for the synthesis of most other types of organotin compounds. Their versatility is illustrated in Scheme 3.

Scheme 3



X = halogen or pseudohalogen

A number of the cleavage reactions described above (especially in Section 3.3.1) yield this class of compound. Interconversion of the halides is usually carried out by treating the chloride with the appropriate salt MX in acetone (X = Cl, Br, I) when MCl precipitates, or in water (X = F) when the tin fluoride precipitates (M = K, Na, NH_4, etc.) (eq. 3-16).

$$R_nSnCl_{4-n} + (4-n)MX \longrightarrow R_nSnX_{4-n} + (4-n)MCl \qquad (3\text{-}16)$$

Essentially the same procedure is used for the preparation of the organotin pseudohalides. In that case, MX can be NaSCN, NaN_3, etc.

Less important general routes are exemplified by the following (eqs. 3-17, 3-18):

$$R_3SnOH + HX \longrightarrow R_3SnX + H_2O \qquad (3\text{-}17)$$

$$R_3SnH + HX\ (\text{or } X_2) \longrightarrow R_3SnX + H_2\ (\text{or HX}) \qquad (3\text{-}18)$$

Some other reactions used for the preparation of the compounds R_3SnX, R_2SnX_2 and $RSnX_3$ are described next.

3.4.1 SYNTHESIS OF R_3SnX COMPOUNDS

The direct reaction of benzyl chloride (uncatalyzed) with tin in water is an exception in this case as it produces high yields of the monochloride (eqs. 3-19, 3-20) (Sisido and Kozima 1968).

$$2C_6H_5CH_2Cl + Sn \longrightarrow (C_6H_5CH_2)_2SnCl_2 \qquad (3\text{-}19)$$

$$3(C_6H_5CH_2)_2SnCl_2 + Sn \longrightarrow 2(C_6H_5CH_2)_3SnCl + 2SnCl_2 \qquad (3\text{-}20)$$

Bulky Grignard reagents sometimes yield the monohalides R_3SnX (see Scheme 2) ($R = C_6H_5(CH_3)_2CCH_2^-$, neophyl group, is another important example; Reichle 1966).

3.4.2 SYNTHESIS OF R_2SnX_2 COMPOUNDS

As indicated in the introduction, the direct synthesis has been known for a long time and is used commercially for $(CH_3)_2SnCl_2$. The reaction requires a catalyst such as $CH_3(C_6H_5)_3P^+Br^-$. The order of reactivity with tin is RI > RBr > RCl, with small R groups reacting more quickly than large R groups.

An important, conceptually related reaction is shown in eq. 3-21 (Davies and Smith 1982), although it probably proceeds via hydrostannation (cf. eq. 3-7). The product is an intermediate for PVC stabilizers.

$$2(n\text{-}C_4H_9OOCCH{=}CH_2) + 2HCl + Sn \longrightarrow (n\text{-}C_4H_9OOCCH_2CH_2)_2SnCl_2 \qquad (3\text{-}21)$$

Less important routes are shown in eqs. 3-22 and 3-23. Note that the very bulky t-butyl group gives an even lower degree of substitution (eq. 3-23) (Kandil and Allred 1970).

$$R_2Hg + SnCl_2 \longrightarrow R_2SnCl_2 + Hg \qquad (3\text{-}22)$$

$$2(CH_3)_3CMgCl + SnCl_4 \longrightarrow ((CH_3)_3C)_2SnCl_2 + 2MgCl_2 \qquad (3\text{-}23)$$

3.4.3 SYNTHESIS OF $RSnX_3$ COMPOUNDS

Tin(II) derivatives oxidatively add alkyl halides (eqs. 3-24, 3-25) (Bulten et al. 1976), the latter being an example of the Meyer reaction.

$$RX + SnX_2 \longrightarrow RSnX_3 \qquad (3\text{-}24)$$

$$RX + K_2SnO_2 \longrightarrow RSnOOK + KX \qquad (3\text{-}25)$$

A catalyst is necessary for the additions to SnX_2 (eq. 3-24) ($(C_6H_5)_3Sb$ is often used), which proceed in the order of reactivity RI > RBr > RCl; $SnI_2 > SnBr_2 > SnCl_2$; $CH_3 > C_2H_5$ > more bulky groups. Again there is a formal analogy with the useful reaction shown in eq. 3-26 (Hutton et al. 1978) (cf. eq. 3-21).

$$ROOCCH{=}CH_2 + HCl + SnCl_2 \longrightarrow ROOCCH_2CH_2SnCl_3 \qquad (3\text{-}26)$$

The synthesis of methyltin triiodide by the reaction of tin sulfide with methyl iodide has been performed (Manders et al. 1984).

3.5 COMPOUNDS WITH TIN-OXYGEN BONDS (Sn-OH, Sn-O-Sn, Sn-OR)

As indicated in Scheme 3, hydroxides are the initial products of the base hydrolysis of the appropriate halide. The monohalides initially afford the hydroxides which in most cases are readily dehydrated to the oxides (eqs. 3-27, 3-28).

$$R_3SnX + NaOH \longrightarrow R_3SnOH + NaX \qquad (3\text{-}27)$$

$$2R_3SnOH \rightleftarrows R_3SnOSnR_3 + H_2O \qquad (3\text{-}28)$$

The ease of oxide formation varies considerably from spontaneous ($R = n\text{-}C_4H_9$) or difficult ($R = (C_6H_5)(CH_3)_2CCH_2^-$), to the spontaneous hydration of oxide to afford the hydroxide in the case of $R = CH_3$ (Davies and Smith 1982).

On hydrolysis, dihalides afford polymeric oxides, possibly via the intermediates shown in eq. 3-29.

$$\begin{tikzcd}
xR_2SnX_2 + 2xNaOH \arrow[r] \arrow[d] & 2xNaX + xH_2O + (R_2SnO)_x & \\
xR_2SnX(OH) \arrow[r] & \frac{x}{2}\ XR_2SnOSnR_2X \arrow[r] & \frac{x}{2}\ XR_2SnOSnR_2OH \arrow[ul]
\end{tikzcd} \qquad (3\text{-}29)$$

Trihalides seem to be hydrolyzed in a similar stepwise manner with the ultimate product being the stannonic acid (eq. 3-30).

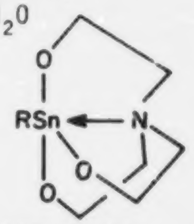
$$RSnX_3 \rightarrow RSn(OH)X_2 \rightarrow RSn(OH)_2X \rightarrow (X(OH)RSn)_2O \rightarrow RSnO(OH) \qquad (3\text{-}30)$$

Alkoxides are obtained in essentially the same manner (eq. 3-31); however, preparation from the oxide is often more convenient as shown in eqs. 3-32 and 3-33 (Saruto and Yukikazu 1966; Davies et al. 1971, 1972). (Note the silatrane analogue of eq. 3-33.)

$$R_2SnCl_2 + 2R^1ONa \longrightarrow R_2Sn(OR^1)_2 + 2NaCl \qquad (3\text{-}31)$$

$$((n\text{-}C_4H_9)_3Sn)_2O + 2n\text{-}C_4H_9OCH_2CH_2OH \longrightarrow$$
$$2(n\text{-}C_4H_9)_3SnOCH_2CH_2OC_4H_9\text{-}n + H_2O \qquad (3\text{-}32)$$

$$RSn(O)OH + (HOCH_2CH_2)_3N \longrightarrow$$



(3-33)

The organotin compounds described in this section undergo a number of reactions of interest in organic synthesis, often by addition across saturated and unsaturated bonds (Bloodworth 1972) (eq. 3-34).

$$\overset{\delta^+}{Sn}\text{-}\overset{\delta^-}{O} + \overset{\delta^-}{A}=\overset{\delta^+}{B} \rightleftarrows Sn\text{-}A\text{-}B\text{-}O \qquad (3\text{-}34)$$

The example given in eq. 3-35 shows the potential for industrial application of this type of compound as a catalyst in polyurethane production (Bloodworth 1972).

$$(n\text{-}C_4H_9)_3SnOC_2H_5 + C_6H_5N{=}C{=}O \rightarrow (n\text{-}C_4H_9)_3SnN(C_6H_5)C(O)OC_2H_5$$

$$(n\text{-}C_4H_9)_3SnN(C_6H_5)C(O)OC_2H_5 + C_2H_5OH \rightarrow (n\text{-}C_4H_9)_3SnOC_2H_5 + C_6H_5NHC(O)OC_2H_5 \qquad (3\text{-}35)$$

3.6 COMPOUNDS WITH TIN-SULFUR BONDS (Sn-S-Sn, Sn-SR)

This is an important class of compounds industrially, and they are prepared by reactions similar to those employed for the tin-oxygen derivatives (Section 3.5). The Sn-S bond is less reactive than the Sn-O bond and the compounds Sn-SH readily eliminate H_2S to afford the sulfide Sn-S-Sn (cf. eq. 3-28). Less obvious methods of preparation are illustrated in eqs. 3-36 and 3-37 (Reichle 1962; Plum and Bokranz 1967).

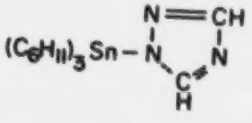
$$(n\text{-}C_4H_9)_2SnCl_2.2C_6H_5NH_2 + 2HSCH_2COO(i\text{-}C_8H_{17}) \longrightarrow (n\text{-}C_4H_9)_2Sn(SCH_2COO(i\text{-}C_8H_{17}))_2 + 2C_6H_5NH_2.HCl \qquad (3\text{-}36)$$

$$((C_6H_5)_3Sn)_2O + CS_2 \longrightarrow (C_6H_5)_3SnOC(S)SSn(C_6H_5)_3 \longrightarrow ((C_6H_5)_3Sn)_2S + COS \qquad (3\text{-}37)$$

The toxic behavior of dialkyltin halides may be due to the formation of $R_2\overline{SnS\text{-}R^1\text{-}S}$ with dithiols such as reduced lipoic acid.

3.7 COMPOUNDS WITH TIN-NITROGEN BONDS

The Sn-N bond is generally very reactive, particularly with protic reagents; consequently, this class of compounds is of marginal interest in the present context. One commercial product is the miticide 1-tricyclohexyltin-1,2,4-triazole (3).



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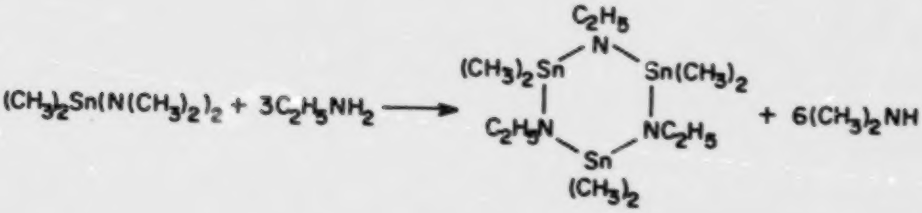
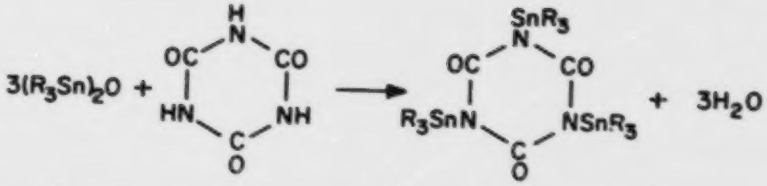
Typical routes to these compounds, and their reactivity patterns, are illustrated in eqs. 3-38 to 3-41 (Reichle 1962; Jones and Lappert 1965; Lappert and Jones 1966; Saruto and Suenobu 1966; Plum and

Bokranz 1967; Tzschach and Reiss 1967; Davies et al. 1971, 1972). If $R^1 = H$ and R^2 = alkyl, the products from eq. 3-38 can condense by elimination of amine.

Synthesis

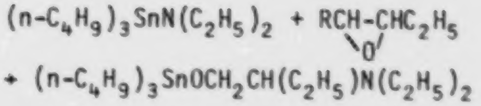
$$R_{4-n}SnCl_n + nLiNR^1R^2 \longrightarrow R_{4-n}SnNR^1R^2 + nLiCl \qquad (3\text{-}38)$$


(3-39)


(3-40)

(See also eq. 3-35.)

Reaction



$$(n\text{-}C_4H_9)_3SnN(C_2H_5)_2 + RCH\text{-}CHC_2H_5 \;(\text{with } O \text{ bridging}) $$

$$\rightarrow (n\text{-}C_4H_9)_3SnOCH_2CH(C_2H_5)N(C_2H_5)_2 \qquad (3\text{-}41)$$

3.8 COMPOUNDS WITH TIN-HYDROGEN BONDS

This class of compound disproportionates in the presence of catalysts (impurities) (eq. 3-42) and is readily oxidized in air to organotin oxides and hydroxides. The compounds are unlikely to exist for long in the environment, although methyl- and butyltin hydrides have been reported (Brinckman et al. 1983). Because of their volatility, they have analytical importance in the speciation of organotin compounds (Braman and Tompkins 1979; Hodge et al. 1979; Chau et al. 1982).

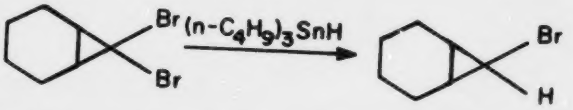
$$4R_nSnH_{4-n} \longrightarrow nR_4Sn + (4-n)Sn + (8-2n)H_2 \qquad (3\text{-}42)$$

The most convenient route to these compounds is by reduction of the appropriate halide by hydride, usually $LiAlH_4$ (eq. 3-43) in ether-like solvents or $NaBH_4$ (in protic solvents).

$$2R_3SnCl + LiAlH_4 \longrightarrow 2R_3SnH + LiAlH_2Cl_2 \qquad (3\text{-}43)$$

Poly(methylhydrosiloxane) easily reduces bis(tributyltin) oxide (Hayashi *et al.* 1967).

The tin hydrides have applications in synthesis (e.g. hydrostannation; eq. 3-7) (reactions usually require a free radical initiator) and reduction of organic halides (hydrostannolysis, e.g. eq. 3-44) (Seyferth *et al.* 1963).



(3-44)

Two other typical reactions follow (eqs. 3-45, 3-46) (Kuivila and Levins 1964; Neumann *et al.* 1967).

$$2R_3SnH \xrightarrow[\text{catalyst}]{\text{amine}} R_3Sn\text{-}SnR_3 + H_2 \qquad (3\text{-}45)$$

$$R_3SnH + CCl_3COOH \longrightarrow R_3SnOOCCCl_3 + H_2 \qquad (3\text{-}46)$$

3.9 COMPOUNDS WITH TIN-METAL BONDS

The main compounds of interest in this category are those that contain Sn-Sn bonds. The tendency of tin to catenate is less significant than that of carbon or indeed silicon. There is no satisfactory explanation for the low thermodynamic stability of these compounds; all, however, are highly reactive and are unlikely to be encountered in the environment.

Routes to the two main classes of these compounds, Sn_xR_{x+2} (open chain) and $(SnR_2)_x$ (cyclic) (x = 9 maximum), are shown in eqs. 3-47 to 3-50 (Tamborski and Soloski 1961; Neumann *et al.* 1965; Sommer *et al.* 1966; Neumann and Koenig 1966; Masamune *et al.* 1983).

$$R_3SnLi + R^1{}_3SnBr \longrightarrow R_3Sn\text{-}SnR^1{}_3 \qquad (3\text{-}47)$$

$$\begin{array}{l} 2(C_6H_5)_3SnN(C_2H_5)_2 + (i\text{-}C_4H_9)_2SnH_2 \longrightarrow \\ \quad (C_6H_5)_3Sn\text{-}Sn(i\text{-}C_4H_9)_2\text{-}Sn(C_6H_5)_3 \end{array} \qquad (3\text{-}48)$$

$$9(i\text{-}C_4H_9)_2SnH_2 \xrightarrow{C_5H_5N} ((i\text{-}C_4H_9)_2Sn)_9 \qquad (3\text{-}49)$$

$$\begin{array}{l} R_2SnCl_2 \xrightarrow{Na} (R_2Sn)_3 \\ R = 2,6\text{-}(C_2H_5)_2C_6H_4 \end{array} \qquad (3\text{-}50)$$

All the compounds react with halogens and alkyl halide with cleavage of the Sn-Sn bond.

Essentially the same procedures are used for the synthesis of other metal derivatives (eqs. 3-51 and 3-52) (Breitschaft and Basolo 1966; Knox et al. 1969).

$$R_3SnCl + Li \rightarrow R_3SnLi \xrightarrow{(n^5\text{-}C_5H_5)_2MCl_2} (n^5\text{-}C_5H_5)_2M(SnR_3)_2 \quad (3\text{-}51)$$

$$M = Ti,\ Hf;\ R = C_6H_5$$

$$(CH_3)_3SnCl + NaCo(CO)_4 \longrightarrow (CH_3)_3SnCo(CO)_4 \quad (3\text{-}52)$$

3.10 ORGANOTIN ESTERS

This is probably the most important class of organotin compounds from an industrial point of view. They are almost invariably prepared from the appropriate chloride or oxide as in eqs. 3-53 and 3-54 (Alleston and Davies 1962; Nakanishi and Inamasu 1967a, b).

$$((n\text{-}C_4H_9)_3Sn)_2O + RR^1C{=}NOCH_2COOH \rightarrow 2(n\text{-}C_4H_9)_3SnOOCCH_2ON{=}CRR^1 + H_2O \quad (3\text{-}53)$$

$$R_nSnCl_{4-n} + (4-n)MOOCR^1 \longrightarrow R_nSn(OOCR^1)_{4-n} + (4-n)HCl \quad (3\text{-}54)$$

$$M = Ag,\ Na,\ K$$

These routes can be generalized to give esters of other acids by using, for example, HNO_3 or $AgNO_3$.

Examples of other more specific syntheses are given in eqs. 3-55 to 3-57 (Mufti and Poller 1967; Lindner et al. 1970; Yeager and Castelli 1978).

$$(n\text{-}C_4H_9)_2SnBr_2 + (n\text{-}C_4H_9)_2Sn(OOCCH_3)_2 \longrightarrow 2(n\text{-}C_4H_9)_2Sn(OOCCH_3)Br \quad (3\text{-}55)$$

$$(n\text{-}C_4H_9)_3SnOOCC(CH_3){=}CH_2 \longrightarrow [-(n\text{-}C_4H_9)_3SnC(CH_3)\text{-}CH_2\text{-}]_x \quad (3\text{-}56)$$

$$R_4Sn + SO_2 \longrightarrow R_3SnOSOR \quad (3\text{-}57)$$

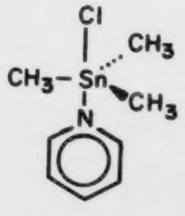
Polymers, like the product from eq. 3-56, have important industrial application in biocidal paints for protecting ships' hulls.

3.11 THE LEWIS ACID CHARACTER AND STRUCTURES OF ORGANOTIN COMPOUNDS

The well-known tendency of $SnCl_4$ to form donor-acceptor complexes ($SnCl_4.2L$) with Lewis bases (L) (Lewis base = electron pair donor) (Cotton and Wilkinson 1972; Huheey 1978) is carried over into the organo-derivatives R_nSnX_{4-n} (n = 1-3) where X is an electron-withdrawing group. The ease of adduct formation generally drops off in the series $RSnX_3 > R_2SnX_2 > R_3SnX$; R = $C_6H_5 > CH_3 > C_2H_5 > C_3H_7$; and, when X = halogen or pseudohalogen (the most studied case), NCS ≈ F > Cl > Cr >I (Davies and Smith 1982). Tin(IV) is best classified as a "hard acid" (Cotton and Wilkinson 1972; Huheey 1978) (class A acceptor) and forms more stable adducts with O- and N-donors. This can lead to intramolecular association if X is a halogen or pseudohalogen or is a ligand which has an otherwise uncoordinated O-, N-, or halogen (but not P- or S-) donor atom. Compounds such as $(C_6H_5)_4Sn$, $(CH_3)_3SnH$, and $[(C_6H_5)_3Sn]_2S$ are monomeric with essentially tetrahedral tin atoms. The tin-tin bonded compounds also have structures similar to the corresponding carbon analogues.

3.11.1 THE R_3SnX COMPOUNDS

These molecules generally are weak acceptors and tend to react with monodentate ligands to give 5-coordinate compounds as in 4 (Hulme 1963). Many of the molecules themselves in the solid state have the idealized polymeric structure seen in 5 (Davies and Smith 1982). The miticide 3 (Section 3.7) is a polymer of this sort (Hammann et al. 1978).



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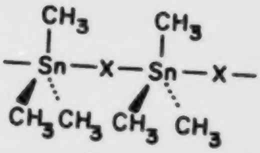

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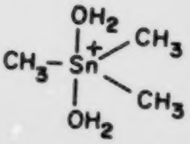
X = F, OH, OC(R)O, OS(R)O



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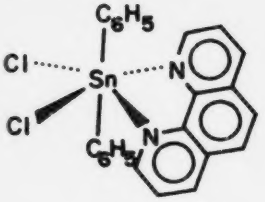
Trimethyltin chloride dissolves in water with the formation of the 5-coordinate cation 6 (Tobias 1978), and related species are ultimately present when any R_3SnX compound dissolves in water (cf. the analogous compounds of the type $[(C_6H_5)_3Sn.2DMSO]^+NO_3^-$ (Simpson 1966)).

It should be noted that most R_3SnX compounds are monomeric in dilute solution (the fluorides of all classes are insoluble in water) and that some, such as $(C_6H_5)_3SnCl$, are monomeric in the solid state (Schlemper 1967; Tobias 1978). This can be attributed to weak Lewis acidity and/or steric effects.

3.11.2 THE R_2SnX_2 COMPOUNDS

The compounds in this class are better acceptors. The central tin atom can achieve 5-, 6-, or 7-coordination by complex formation or intramolecular association. Examples are given in structures 7 to 10.

The 6-coordinate adduct 7 of $(C_6H_5)_2SnCl_2$ has cis chlorine atoms and is structurally similar to the anti-cancer drug cis-$(NH_3)_2PtCl_2$ (Cleare 1974).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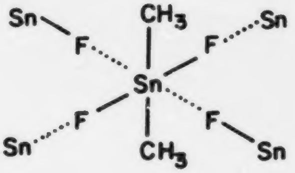
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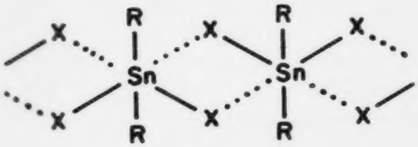
Although 7 is inactive, other closely related compounds exhibit therapeutic activity in vivo towards P-388 lymphocytic leukemia in mice (Crowe et al. 1980, 1984). The structure of $(CH_3)_2SnF_2$ (8) (Schlemper and Hamilton 1966) consists of infinite sheets, whereas that of a number of other derivatives can be represented by the bridged polymer 9 (Davies and Smith 1982).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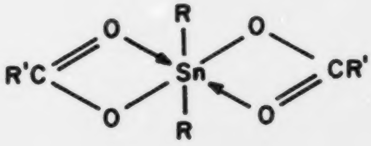
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In solution the dicarboxylates are monomeric and probably have the 6-coordinate structure 10 (the structure of $(CH_3)_2SnCl(OOCCH_3)$ is similar to structure 5; Allen et al. 1981); they are partially hydrolyzed to dimeric compounds such as $R_2Sn(OOCR^1)OSnR_2OH$ (Okawara and Ohara 1971).

The structure of dimethyltin dioxinate (11) (Schlemper 1967) is typical of a number of products obtained by reacting R_nSnQ_{4-n} with organic compounds containing OH groups (or their metal salts such as H-oxinate, H-acac or H-tropolone) (eq. 3-59). These compounds have utility in the analysis and speciation of organotin compounds (Poller 1970), although redistribution can be a problem (Craig and Rapsomanikis 1983).

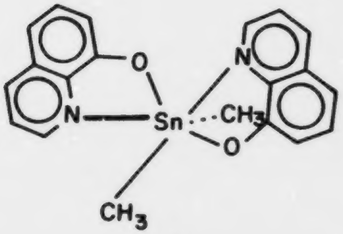
$$(n\text{-}C_4H_9)_2SnCl_2 + 2HOx \longrightarrow (n\text{-}C_4H_9)_2Sn(Ox)_2 + 2HCl \qquad (3\text{-}59)$$

where Ox = oxinate

Water-soluble R_2SnQ_2 compounds are probably present in solution as a variety of species ranging from $R_2Sn(H_2O)_4^{2+}$ to $R_2Sn(OH)_2(aq)$ and $R_2SnOH^+(aq)$.

The disproportionation reactions in eq. 3-60 should be noted (Tobias and Friedline 1965).

$$3(CH_3)_2Sn^{2+} \xrightarrow[\substack{H_2O \\ \text{strong base}}]{2OH^-} 3(CH_3)_2Sn(OH)_4^{2-} \xrightarrow{\text{slow}} 2(CH_3)_3SnOH + Sn(OH)_6^{2-} + 4OH^- \qquad (3\text{-}60)$$



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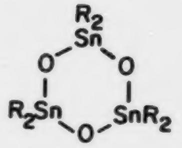


12

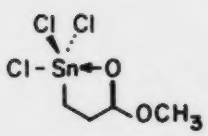
The ultimate hydrolysis products of many compounds R_2SnX_2 are the oxides R_2SnO. These seem to be as yet poorly characterized cross-linked polymers, except in the case of bulky R groups where species of low molecular weight such as the trimer 12 (Masamune et al. 1983) can be isolated.

3.11.3 THE $RSnX_3$ COMPOUNDS

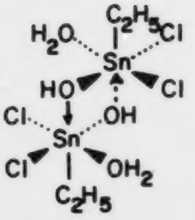
Coordination numbers greater than 4 are the rule for $RSnX_3$ compounds, with seven being the upper limit as in the nitrate (1) (Brownlee et al. 1971).

In this class, as in the previous one, intermolecular chelate formation can occur if the ligand has a suitably placed group which can coordinate as in 13 (Harrison et al. 1979) and the silatrane analogue (eq. 3-33).

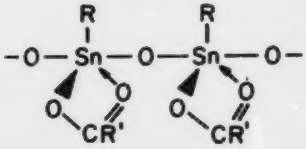
Hydrolysis of these compounds can occur in a stepwise fashion (as for the R_2SnX_2 class) with the ultimate product being the polymeric RSnO(OH). Some intermediates have been isolated from hydrolysis of the carboxylates and chlorides (Okawara and Ohara 1971). For example, 14 is one of the monohydrates $RSn(OH)Cl_2.H_2O$ (Lecomte et al. 1976) that are easily formed from the chlorides $RSnCl_3$. The structure 15 was deduced from Mössbauer spectroscopy; such products are the results of facile hydrolysis of the tricarboxylates (Ford et al. 1969).


Cl
Cl
Cl
Sn
O
OCH3

13


H2O
C2H5
Cl
Sn
HO
Cl
Cl
OH
Sn
Cl
OH2
C2H5

14


R
R
O
Sn
O
Sn
O
O
O
CR'
O
O
CR'

15

4.0 ANALYTICAL APPROACHES

4.1 HISTORICAL NOTES

The analytical chemistry of tin is essentially a product of this century, with the first references dating from the early 1900's (e.g. Andrews 1903, cited by Price 1962). Early methods were classical gravimetric or volumetric procedures which were used to assay for total tin in foodstuffs, metallurgical products and geological samples. Optical spectrographic analysis for total tin was used extensively for geological studies as early as 1931 (Noddack and Noddack 1931, cited by Wedepohl 1972) and was probably the method of choice for similar applications into the 1960's. Development of more sensitive and specific colorimetric, fluorimetric and nuclear activation procedures (e.g. Onishi and Sandell 1956, 1957; Hamaguchi et al. 1964) replaced the spectrographic procedures of the late 1950's and early 1960's. Although flame atomic absorption techniques were also developed in this time period, other methods remained more popular owing to the low sensitivity of tin absorption lines.

The analytical chemistry of organotin compounds dates back to the mid-1920's. From then until the 1950's, applications were to elemental analysis and structure determinations (see Crompton 1974 and references therein). Determination of the tin was by known methods for the inorganic form, after degradation of the organotin compound in mineral acids and ignition (Kocheshkov 1926). The development of instrumental procedures such as gas chromatography and polarography was paralleled by the synthesis of thousands of new organotin compounds, many of which found application as pesticides, plasticizers and antioxidants. It was at this time that residue analysis became important and methods to quantify organotin compounds at microgram levels evolved. The area of pesticide residues, in particular, received close attention because of a need to know the distribution and fate of, for example, fungicides in foodstuffs and in the terrestrial ecosystem (see Kumpulainen and Koivistoinen 1977, who review pesticide residue analysis up to the middle of the last decade). It has been only in the last half-decade that hydrospheric analysis has become sensitive and specific enough to be practical.

The great emphasis on quantitative analysis has caused little attention to be given to the qualitative aspects of tin and organotin chemistry in an environmental context. Historically, the classical separation techniques and spot tests have been used to identify tin in alloys, geological samples, and in chemical mixtures of unknown composition (Charlot 1954). In the past 30 years instrumental methods such as infrared spectrometry, nuclear magnetic resonance techniques and Mössbauer spectrometry have been used to characterize tin compounds and provide information on their molecular structures (see Crompton 1974 for a review of these techniques). These methods have understandably received little attention from environmental chemists because they lack the sensitivity at the nanomolar to picomolar concentrations now known to exist. It can also be seen that the existing quantitative methods can provide initial information on the presence or absence of tin species. This is not to say that there is no potential for the development of spot tests or rapid instrumental methods which may provide qualitative information when the need to quantify does not exist or is more costly. For example, Arakawa et al. (1983) found that the fluorescence detection of the Morin complex of dialkyltin compounds was sensitive to 1.0 $\mathrm{nmol.L^{-1}}$ of the compounds. Such methods would obviously require specificity as well.

4.2 QUANTITATIVE TECHNIQUES

Organotin compounds exist in the environment in both molecular and ionic forms, and are also incorporated into large molecules of biological origin. The molecular forms such as tetraalkyltin and alkyltin hydrides are relatively volatile. The aquated and ionic forms are mono-, di- and trialkylsubstituted tin(IV) of the form $R_nSnQ_{(4-n)}$; they are polar and remain as ionic forms in solution or in sediment. Because of their differing degrees of substitution and lengths of the alkyl groups, all these chemical species exhibit different chemical and physical behavior. For environmental investigations, sensitive and species-specific methods are required.

Several techniques are available for organotin analysis. These techniques and their detection limits are summarized in Table 4-1. Appendix IV.0 describes in more detail those analytical methods for organotin species which are relevant to the aquatic environment, with specific comments on methods, where appropriate. In many cases these methods are also suitable for inorganic tin and for organotin compounds in media distinct from aquatic environments. Compounds (in Appendix IV.0) have been designated for convenience as cations, since there is evidence that at least some organotin species exist as cations (e.g. Tobias 1966; Maguire et al. 1983). Where it is obvious that an ion is not involved (e.g. neat compound analysis), the appropriate compound is noted. In addition, the figures in the column of detection limits in Table 4-1 and Appendix IV.0 should be regarded with caution since it is not yet common practice, however desirable, to distinguish "limit of detection" from "limit of quantitation." In this regard, the American Chemical Society (1983) has published a good review, with guidelines.

The National Bureau of Standards in Washington, D.C., is currently conducting an interlaboratory comparison of test methods for the determination of tributyltin compounds (Blair 1984).

4.2.1 SPECTROPHOTOMETRY/SPECTROFLUORIMETRY

The earliest spectrophotometric method for organotin analysis was probably the dithizone method (Aldridge and Cremer 1957). Both the

Table 4-1. Summary of techniques for analysis of organotin compounds.

Technique[α]	Analyte form	Detection limit[β] (Sn)
Spectrophotometry	R_2SnQ_2, R_3SnQ	
Spectrofluorimetry	$R_nSnQ_{(4-n)}$, ϕ_3SnQ (R = Me, Et, Pr, Bu)	10^{-9} - 10^{-7} mol.L^{-1}
ASV	ϕ_3SnQ $BuSnCl_3$, $OcSnCl_3$, $SnCl_4$	10^{-8} mol.L^{-1} 3 x 10^{-7} mol.L^{-1}
GC-ECD	R_3SnQ, R_4Sn (R = Et, Pr, Bu)	8.40 x 10^{-15} - 8.40 x 10^{-11} mol
GC-FPD	R_nSnH_{4-n} (R = Me, Bu, ϕ)	4.20 x 10^{-13} mol
GC-FPD modified	Pr_4Sn	3.36 x 10^{-16} mol
GC-AAS	Me_nSnBu_{4-n}	8.40 x 10^{-13} mol
GC-emission	Me_nSnH_{4-n}	8.40 x 10^{-14} mol
GC-plasma	Et_nSnPr_{4-n}	5.04 x 10^{-14} mol
GC-MS	Bu_nSnMe_{4-n}	1.68 x 10^{-12} mol
GC-FID	R_4Sn (R = Et, Pr, Bu)	8.40 x 10^{-12} mol
LC-AAS	R_nSnH_{4-n} (R = Me, Et)	8.40 x 10^{-14} mol
LC-AAS	$R_nS_nQ_{4-n}$ (R = aryl, alkyl and alicyclic)	2.52 x 10^{-12} - 4.20 x 10^{-11} mol
TLC-AAS	Bu_3SnQ, ϕ_3SnQ	1.68 x 10^{-9} mol

[α] Abbreviations are as follows: ASV, anodic stripping voltammetry; ECD, electron capture detector; GC, gas chromatography; FPD, flame photometric detector; AAS, atomic absorption spectrometry; MS, mass spectrometry; FID, flame ionization detector; LC, liquid chromatography; TLC, thin-layer chromatography; Me, methyl; Et, ethyl; Pr, propyl; Bu, butyl; Oc, octyl; ϕ, phenyl; Q is the counterion.

[β] Detection limits are in moles of Sn and are reported as those amounts or concentrations that generate a signal twice the baseline noise.

diethyltin and triethyltin chlorides react with dithizone to form colored complexes. The diethyltin and triethyltin species in chloroform are shaken with potassium hydroxide; the diethyltin species partition into the alkali while most of the triethyltin species pass into the chloroform. Separation is also obtained between chloroform and borate buffer with or without EDTA. Other dialkyltin and trialkyltin species have similar absorption spectra. The method is sensitive and it differentiates the dialkyltin and trialkyltin species without determining the identity of the alkyl groups.

The use of the reagent diphenylcarbazone was later developed for dibutyltin dichloride (Skeel and Bricker 1961), with sensitivity in the microgram range. Other colorimetric reagents, including dithiol, hematoxylin, 8-hydroxyquinoline, phenylfluorone (Farnsworth and Pekola 1961) and pyrocatechol violet (Ross and White 1961a, b; Omar and Bowen 1982), have been used. All these colorimetric reagents form complexes with inorganic tin and many other metals. For organotin analysis, the sample generally has to be digested to convert all the tin to the inorganic form before the color development. Because of the lack of specificity of the colorimetric methods, an efficient separation of tin compounds is necessary before its measurement. The dithizone method after modification can selectively extract the trialkyltin compounds from alkaline medium by chlorobenzene in the presence of a complexing agent, under which conditions the mono- and dialkyltin compounds and all the interfering ions are not extractable (Havir and Vrestal 1972). This is perhaps the best modified dithizone method.

Fluorimetric techniques are in general more sensitive. The most widely used reagent for spectrofluorimetry is 3-hydroxyflavone, which has been applied to the determination of triphenyltin species in potatoes (Vernon 1974) and in water (Blunden and Chapman 1978). Concentrations as low as 0.004 $mg.L^{-1}$ of triphenyltin species (~10 $nmol.L^{-1}$ Sn) in water can readily be determined. In combination with the dithizone reagent, 3-hydroxyflavone can be used to determine mixtures of dimethyltin and trimethyltin in aqueous solutions (Aldridge and Street 1981). Other fluorimetric agents, for example, Morin (2',3,4',5,7-pentahydroxyflavone), have been used for alkyltin and phenyltin compounds (Arakawa et al. 1983).

4.2.2 ELECTROCHEMISTRY

Electrochemical techniques, including polarography, anodic stripping voltammetry (ASV) and potentiometric titrations, have been applied to the determination of concentrations of organotin compounds in nonaqueous and aqueous media. Triphenyltin has been determined by ASV (Booth and Fleet 1970) and potentiometric titrations (Litan et al. 1978). The ASV method is generally more sensitive than any other electrochemical method and reaches a detection limit of 0.01 $\mu mol.L^{-1}$. The ASV method has also been applied to other industrial tin and organotin compounds, such as butyltin trichloride, octyltin trichloride, benzylstannic acid, dibenzyltin dichloride and stannic chloride, with minimum detectable concentrations about 0.3 µmol.L^{-1} (Woggon et al. 1972). Other techniques include differential pulse polarographic determination of tributyltin and dibutyltin species used for coating fishing nets (Hasebe et al. 1982) and pulse polarography for tributyltin species leached out from paints (Battais et al. 1982).

Electrochemical methods are sensitive in the general sense but are still not sensitive enough to meet the demand of organotin analysis in natural water in the picomole per litre range. Although electrochemical methods can differentiate species according to their redox potentials, they are not considered specific techniques. Furthermore, because of the serious problems of interference by organic matter present in water which coats the electrodes, broadens the peaks and sometimes shifts the peak potentials, electrochemical techniques have limited use in the analysis of natural water, especially in polluted samples with complex matrices.

4.2.3 ATOMIC SPECTROMETRY

Atomic absorption (AAS) or atomic emission spectrometric techniques do not offer information on the speciation of the analyte; they can only determine total tin atoms in the sample. Normally the organotin compounds are digested in acids or extracted into solvents before they are introduced to the atomization device, either a flame (Marr and Anwar 1982) or an electrically heated graphite furnace (Varnes and Gaylor 1978). Mixtures of dibutyltin and tributyltin species have been separated by solvent partition before the graphite furnace - AAS analysis (Kojima 1979). Coating the graphite furnace interior with a refractory metal salt such as zirconyl acetate increases the atomization efficiency of tin (Vickrey et al. 1981). It has been observed that a relationship exists between the atomic absorption sensitivity and structure of the compound for a number of organotin compounds (Peetre and Smith 1974); it is therefore necessary, for practical purposes, to convert all compounds into the same form before determination by atomic absorption.

There is not much literature on the emission spectrometric determination of tin. For high sensitivity work, plasma emission has been used as a detector in conjunction with gas chromatographic separation for a variety of tetraalkyltin compounds (Estes et al. 1982).

4.2.4 GAS CHROMATOGRAPHY

For the gas chromatographic (GC) separation of organotin compounds, the analytes must be volatile or rendered volatile so that they can be separated in the chromatographic column. For the polar and aquated alkyltin ions, R_nSnQ_{4-n}, a derivatization technique is normally employed to convert them to volatile species prior to the GC separation. Two derivatization techniques have been commonly used.

(i) Formation of hydrides

Excess borohydride reagent is used to convert the cationic alkyltin species in situ to their corresponding hydrides, R_nSnH_{4-n}, which can be purged from solution with an inert gas and collected in a cold trap or chromatographic column prior to elution into the detector. Alternatively, an organotin-containing organic extract can be concentrated to a small volume before hydride derivatives are prepared, and samples of the resulting solution can be analyzed by GC (Soderquist and Crosby 1978). Under some conditions the hydride derivatives are not stable in this latter "batch" mode (Soderquist and Crosby 1978) or in the former in situ generation mode (Chau 1983).

(ii) Alkylation with a Grignard reagent

The reaction of Grignard reagents in organometallic chemistry is well known. The reaction of monoalkyl-, dialkyl- or trialkyltin species and a Grignard reagent readily and quantitatively proceeds to completion at very low concentrations, with no rearrangement of the original alkyl groups attached to the tin nucleus which would obscure the original speciation (Neubert and Wirth 1975). Alkyltin derivatives ($R_nSnR'_{4-n}$) cannot be prepared in situ. The usual technique is to extract large volumes or amounts of sample, prepare derivatives, "clean up" interferences as necessary, reduce the organic solution to a small volume (1 mL or less) and inject a sample into the GC. Such tetraalkyltin derivatives are in general quite stable in organic solvents (Neubert and Wirth 1975; Maguire and Huneault 1981).

Mass spectrometric (MS), electron capture (EC) and flame photometric detectors are the most sensitive of the conventional GC detectors that have been used for the determination of organotin compounds. Methylbutyltin species have been detected by GC-MS (Meinema et al. 1978). Phenyltin hydrides have been determined by GC-EC (Soderquist and Crosby 1978).

The flame photometric detector (FPD) is perhaps the most sensitive detector used for the gas chromatographic analysis for tin, especially those models with glass internal surfaces. Modification of the flame photometric detector has enhanced its response to tin, with detection limits now as low as 5×10^{-18} mol tin per second (Aue and Flinn 1980). However, the refractory combustion product SnO_2 may accumulate on internal surfaces, causing a decrease in detector sensitivity (e.g. Maguire and Tkacz 1983). In addition, the detector is easily "poisoned" by tropolone which is used in extracting butyltin species from water or sediment (Maguire and Tkacz 1983). The FPD has been used as a tin-selective detector for GC determination of butyltin species in water (Maguire and Huneault 1981) and sediment (Maguire 1984), and methyltin species in water (Braman and Tompkins 1979).

The combination of gas chromatographic separation with element-specific detection has been widely used in the determination of a wide variety of organometallic compounds, including organotin compounds. Atomic absorption has been the most widely chosen element-specific detection system for use with GC (Hodge et al. 1979; Chau et al. 1982; Andreae 1983). Methyltin species in natural waters have been determined after hydride derivatization with an atomic absorption spectrometer with a quartz tube furnace (Hodge et al. 1979), and an atomic absorption spectrometer with a graphite furnace (Andreae 1983). The quartz tube furnace - AAS technique, introduced by Chu et al. (1972), has the advantages that fouled furnaces are disposable and that the technique may be used for many different volatile metals or organometals. The graphite furnace - AAS method features introduction of the hydrides with the carrier gas stream (with supplemental argon) into the internal purge inlet of the graphite furnace. The hydrides pass through the graphite tube and the reaction products leave through the internal purge outlet. Although this technique works well with the very volatile methyltin hydrides, less volatile hydrides of butyltin and phenyltin species may condense on the relatively cool inner surfaces of the graphite furnace assembly before getting to the furnace. The GC-AAS technique is also suitable for determination of tetraalkyltin compounds (Chau et al. 1982).

As stated above, a plasma emission spectrometer has been used as a detector in conjunction with a gas chromatograph in the determination of a variety of tetraalkyltin compounds (Estes et al. 1982).

Direct determination of tetraalkyltin compounds in various biological materials by gas chromatography with a detection limit of 8.40×10^{-7} $mol.kg^{-1}$ tissue has been carried out with a hydrogen flame ionization detector (FID) (Arakawa et al. 1981b). The extraction was modified by using a more polar solvent, ethyl acetate, to recover the polar trialkyltin compounds (Arakawa et al. 1981a). With an electron capture detector (ECD), 8.40×10^{-9} $mol.kg^{-1}$ of tissue can be detected.

4.2.5 LIQUID CHROMATOGRAPHY

Liquid chromatographic (LC) separation of organotin compounds does not, of course, require the preparation of volatile analytes, and would in general be the method of choice for analysis of nonvolatile or high-molecular-weight organotin compounds were it not for the fact that the development of sensitive detectors has been slower than in the field of gas chromatography. Many problems associated with combining the liquid chromatograph with a furnace and with solvent interferences of the plasma still remain to be solved. With flame AAS as the detector, the LC effluent can be fed directly into the burner nebulizer. An auxiliary solvent flow may be required to balance the nebulizer gas flow. However, the flame mode of AA operation is not desirable for most speciation work in environmental studies. Electrothermal furnaces can generally provide detection limits three orders of magnitude lower than those of flame atomizers.

There are two basic approaches to solving the difficulties in efficiently combining the furnace AAS with a liquid chromatograph. The first approach is to install a sampling device between the LC and the AA furnace to sample the effluent and inject it into the furnace. The major drawback of this interface is the lengthy analysis time because of the cycles required in the furnace operation. Commercial auto-samplers have been used to connect high-performance liquid chromatography (HPLC) and the graphite furnace AA spectrometer in the speciation of di- and triorganotin compounds in water (Jewett and Brinckman 1981). Such an interface results in pulse signals, the sum of which can be taken to calculate the amount of analyte. Because the sampling rate is dependent upon the rate of graphite furnace operation, which generally consists of three cycles plus cooling time (about 30-40 s per sample), only broad chromatographic peaks can be analyzed. The synchronization of the auto-sampler to the position of the peak in the LC flow is crucial in the optimization of operation. Current improvements include storage of the chromatographic peaks for more detailed analysis of the peak-containing aliquot off-line. Thus the number of AA analyses is no longer limited by the flow rate nor restricted by the furnace cycles (Vickrey et al. 1980a). This technique has been used to speciate several dialkyl- and trialkyltin compounds. Although lengthy, this technique certainly improves the description of a chromatographic peak.

The second approach to connecting the furnace with the LC includes the conversion of the analytes on-line to volatile derivatives for continuous feeding to the furnace after gas-liquid separation. For elements that readily form covalent hydrides, such as As(III), As(V), Ge(IV), Sn(IV), Pb(IV) and Sb (V), this on-line hydride generation technique has achieved a great degree of success. The technique has been applied to the determination of methyltin species after conversion to their hydrides with excellent sensitivity (2-20 pg) (Burns et al. 1981). This system is currently the state-of-the-art of LC-AAS interfacing. It remains to be seen if this technique is successful with larger organotin molecules.

Another technique of promise is the coupling of a microbore HPLC to a flame photometric detector or a quartz tube furnace - AAS. The small solvent flow rate (10-100 $\mu L.min^{-1}$) in microbore HPLC has already been shown to be compatible with direct introduction to flame photometric and alkaline flame ionization detectors in the analysis of organophosphorus pesticides (McGuffin and Novotny 1981a, b).

4.3 APPLICATIONS TO ENVIRONMENTAL SAMPLING

Investigations of the occurrence of organotin compounds in environmental samples began relatively recently. The lack of suitable methods is reflected by the paucity of environmental data. All the above methods are applicable to the analysis of water. The combination of separation technique and element-specific detector, such as GC-AAS or HPLC-AAS, is the obvious choice for speciation analysis of organotin compounds. Methods for the determination of organotin species in water were reviewed in previous sections.

There are few reports on the analysis of sediment or biota for organotin compounds. Seidel et al. (1980) used 0.3 N HCl to extract sediment and analyzed the leachate by the hydride generation technique. No evaluation of the recovery of alkyltin compounds was given and the efficiency of the dilute acid extraction is not known. Chau et al. (1984) developed an extraction method using a solution of tropolone in benzene for methyltin species in sediment in the presence of saturated sodium chloride. After separation the extract is butylated with butyl Grignard reagent to convert the methyltin species to the butyl derivatives for GC-AAS analysis. A similar approach was taken for aquatic biota including fish. The digestion of the biological tissues without rupturing carbon-tin bonds was accomplished with tetramethylammonium hydroxide. The recovery of the mono-, di- and trimethyltin chloride in spiked fish samples is satisfactory. An environmental survey of the methyltin species in aquatic biota is in progress (Chau et al. 1984).

Maguire (1984) developed an extraction technique for butyltin species in sediment using tropolone in benzene. After the mixture is refluxed for 2 h, the extract is pentylated with pentyl Grignard reagent to convert the butyltin to tetrasubstituted butyl-pentyl derivatives. The extract can be concentrated by evaporation at reduced pressure for GC-AAS analysis. The recoveries for the butyltin species are satisfactory.

5.0 ENVIRONMENTAL OCCURRENCE AND TRANSFORMATIONS

Appendix V.0 shows the aquatic environmental occurrence of tin and organotin compounds. There are few data, largely because of the lack of suitable analytical methods for determining organotin species at trace levels in past years. With the rapid development of sensitive analytical techniques (see Chapter 4), organotin compounds can now be determined at environmental concentrations.

5.1 CRUSTAL ABUNDANCE AND GLOBAL DISTRIBUTION OF TIN

The element tin is fairly evenly distributed among crustal rocks. Onishi and Sandell (1957) concluded that the upper lithosphere contained 2 ± 1 $mg.kg^{-1}$ tin equally distributed between granite and mafic rocks (basalts). These results were confirmed by Hamaguchi et al. (1964) in an extensive investigation of tin geochemistry and in studies by Smith and Burton (1972). Concentrations for crustal tin are shown in Table 5-1.

A computer-derived computation of the geochemical balance of tin and 64 other elements in the major lithospheric and hydrospheric compartments was reported by Horn and Adams (1966). Using data available at that time, abundances by lithologic category and four sedimentary domains were calculated (see Appendix VI.0). Of the seven lithologic categories, shales were determined to contain the highest tin concentration, approximately 4 $mg.kg^{-1}$. Within the sedimentary domains tin was evenly distributed (about 2 $mg.kg^{-1}$).

The major natural source of tin in marine water has been identified to be continental weathering and riverine transport to the oceans. Lantzy and Mackenzie (1979) estimated that fluvial transport accounted for 2.9×10^5 $Mg.a^{-1}$ (1 Mg = 1 tonne) of tin. Considering anthropogenic sources, Byrd and Andreae (1982) assumed that ≈20% of world tin consumption (2.4×10^5 $Mg.a^{-1}$) entered rivers and became associated with particulate material. The total particulate flux was estimated to be 8.3×10^4 $Mg.a^{-1}$, compared with a dissolved flux of 2.2×10^2 $Mg.a^{-1}$. Byrd and Andreae (1982) concluded that only dissolved tin in rivers contributes significantly to oceanic mass balance of the element. Since this flux was two orders of magnitude lower than the oceanic scavenging removal flux of 2.2×10^4 $Mg.a^{-1}$, a significant eolian contribution must be assumed to occur. The estimated range for natural inputs of the element into the atmosphere was $(2\text{-}10) \times 10^3$ $Mg.a^{-1}$. Anthropogenic input was estimated to be $(10\text{-}60) \times 10^3$ $Mg.a^{-1}$. Organotin compound contribution to this was calculated as 4×10^2 $Mg.a^{-1}$. From these reports it is apparent that there will be a need for considerably more data before improved flux models can be generated.

Although 18 tin-containing minerals have been identified (Wedepohl 1972), the most important tin ore is cassiterite (SnO_2) which is highly resistant to weathering. Hydrolysis products of tin are

Table 5-1. Crustal concentration and distribution of tin.

Medium	Concentration (mg.kg^{-1})	Reference
Silicic rocks (Japan)	3.6	Hamaguchi *et al.* (1964)
Silicic rocks (general)	2.5	Smith and Burton (1972)
Basalts (mafic) (Japan)	0.9	Hamaguchi *et al.* (1964)
Basalts (general)	1.7	Smith and Burton (1972)
Ultramafic rock (Japan)	0.35	Hamaguchi *et al.* (1964)
Ultramafic rock (general)	0.8	Smith and Burton (1972)
Red clays (Western Pacific Ocean)	4.0	Hamaguchi *et al.* (1964)
Red clays	3.4	Smith and Burton (1972)
Globigerina ooze (Pacific Ocean)	1.5	Hamaguchi *et al.* (1964)
Volcanic muds (Pacific Ocean)	1.4	Hamaguchi *et al.* (1964)
Shales	6	Iverson and Brinckman (1978)

highly insoluble. This fact is reflected in the very low concentrations of dissolved total inorganic tin in seawater. The earliest historical value of 32 $nmol.L^{-1}$ (3.9 $\mu g.L^{-1}$) was reported by Noddack and Noddack (1939). Post World War II values for this parameter steadily decreased as methods improved. The first 'modern' value of 15 $nmol.L^{-1}$ (1.8 $\mu g.L^{-1}$) was reported by Shimizu and Ogata (1963), and a study of Hamaguchi et al. (1964) gave values of 2.5 to 10 $nmol.L^{-1}$ (0.3-1.20 $\mu g.L^{-1}$).

The data of Smith and Burton (1972) were the first to be consistent with values reported currently for total inorganic tin. Values of 67 to 340 $pmol.L^{-1}$ were obtained for coastal and open Atlantic locations. Current data for inorganic Sn are listed in Appendix V.0.

Low solubility of tin minerals is reflected in the amounts reported for inorganic tin in rivers and lakes. Probably among the earliest reports, Kleinkopf (1960) gave a value of 250 $pmol.L^{-1}$ (30 $ng.L^{-1}$ Sn) for Maine lakes. This was at or near the limit of detection for the spectrographic method employed. Contemporary reports place inorganic tin concentrations in the range of 1.7-1036 $pmol.L^{-1}$ (0.2-120 $ng.L^{-1}$ Sn) for 17 U.S. rivers and 2 German rivers (Byrd and Andreae 1982); 0.7-4.1 $nmol.L^{-1}$ (80-490 $ng.L^{-1}$ Sn) for Lake Michigan (Hodge et al. 1979); and an average of 3.5 $pmol.L^{-1}$ (0.42 $ng.L^{-1}$ Sn) for lakes and rivers of Florida (Braman and Tompkins 1979). Total recoverable inorganic tin concentrations for several Canadian freshwater sources are shown in Table 5-2 (Section 5.2).

5.2 ORGANOTIN COMPOUNDS IN FRESH WATER

Methyltin species, which can be derived from anthropogenic sources as well as from biotic and abiotic methylation of inorganic tin and organotin compounds (Chau et al. 1981; Brinckman et al. 1983), have been detected in a variety of natural waters, sediments and rain (Braman and Tompkins 1979; Hodge et al. 1979; Byrd and Andreae 1982; Jackson et al. 1982; Maguire et al. 1982; Tugrul et al. 1983). Butyltin compounds, which occur in close association with harbor locations because of their anthropogenic sources, have been found in lakes, rivers and sediment (Seidel et al. 1980; Maguire et al. 1982; Maguire 1984).

The concentrations of methyltin and butyltin species in the water of lakes and rivers in Ontario are summarized in Tables 5-2 to 5-4. Table 5-2 shows concentrations of the Bu_3Sn^+ species in Collingwood Harbour, a marina in Lake St. Clair, Toronto Harbour and Ramsey Lake which are 15-60% of the 12-d LC_{100} value for rainbow trout yolk sac fry (Seinen et al. 1981). The probable source of the Bu_3Sn^+ species in these locations is antifouling paint on boats, ships and docks.

The species Bu_2Sn^{2+} occurs in 20 of 30 subsurface water samples; it may be derived from the Bu_3Sn^+ species or from poly(vinyl chloride) stabilizers such as dibutyltin bis(isooctyl mercaptoacetate).

Table 5-2. Concentrations of butyltin species and total recoverable inorganic tin (TRIT) in unfiltered subsurface water (from Maguire _et al_. 1982)[α].

Location	Concentration (mol.L^{-1} Sn)			
	Bu_3SnQ	Bu_2SnQ_2	$BuSnQ_3$	TRIT
Lake Superior (Thunder Bay)				
Lake Superior (Red Rock)		4.3×10^{-11}		
Lake Superior (Marathon)	6.9×10^{-11}	2.4×10^{-9}		6.1×10^{-9}
Turkey Lake 1				
Turkey Lake 2				8.9×10^{-9}
Turkey Lake 3				
Turkey Lake 4		3.4×10^{-10}		3.4×10^{-10}
Turkey Lake 5		8.6×10^{-11}		
Sault Ste. Marie Harbour		1.3×10^{-10}		2.0×10^{-8}
Ramsey Lake (Sudbury)	2.6×10^{-9}	8.6×10^{-11}		4.1×10^{-7}
Nepewassi Lake (Sudbury)		3.4×10^{-10}		
Lake Nipissing (North Bay)		1.0×10^{-9}		
Plastic Lake		2.1×10^{-10}		4.1×10^{-9}
Collingwood Harbour	3.5×10^{-9}			4.2×10^{-7}
Owen Sound Harbour		8.6×10^{-11}		2.7×10^{-9}
St. Clair River 1		4.3×10^{-11}		1.0×10^{-9}
St. Clair River 2		1.8×10^{-9}		5.0×10^{-10}
St. Clair River 3		1.3×10^{-9}		5.0×10^{-10}
Lake St. Clair (Mitchell Bay)		8.6×10^{-11}		1.6×10^{-8}
Lake St. Clair (marina)	1.0×10^{-8}	3.1×10^{-8}	4.8×10^{-8}	5.0×10^{-8}
Thames River (400 m upstream from mouth)				5.0×10^{-10}
Port Dover Harbour				8.4×10^{-11}
Grand River (mouth)				1.7×10^{-10}
Hamilton Harbour	5.5×10^{-10}	8.6×10^{-11}	1.1×10^{-10}	6.7×10^{-10}
Toronto Harbour	2.9×10^{-9}	1.2×10^{-9}		8.7×10^{-9}
Whitby Harbour	1.7×10^{-10}	3.9×10^{-10}		1.8×10^{-8}
Belleville Harbour		4.9×10^{-11}		4.5×10^{-9}
Kingston Harbour	3.5×10^{-11}	1.3×10^{-10}		5.7×10^{-9}
St. Lawrence River 1				8.4×10^{-11}
St. Lawrence River 2				8.4×10^{-11}

[α] Q is the counterion; blank means not detected; the minimum detectable concentration of each species is approximately 3.4×10^{-11} mol.L^{-1} Sn.

The species $BuSn^{3+}$ occurs rarely in subsurface waters, but inorganic tin is widespread and especially concentrated in Collingwood Harbour and Ramsey Lake.

The presence of pollutants in high concentrations in surface microlayers is important to surface-dwelling biota and in considerations of air-water exchange. Table 5-3 shows the concentrations of the Bu_3Sn^+ and Bu_2Sn^{2+} species, and of inorganic tin in the surface microlayer, i.e. the top 60 µm of the water column as sampled with a glass plate.

The $BuSn^{3+}$ species was not detected in any surface microlayer sample, but the other three species were concentrated by factors of up to 10^4 in the surface microlayer relative to subsurface water. It was estimated that (i) for Nepewassi Lake and Lake Nipissing, the amounts of inorganic tin in the surface microlayer were >38% and >18%, respectively, of the amounts in the whole depth of subsurface water, and (ii) for Whitby and Belleville Harbours, the amounts of the Bu_2Sn^{2+} species in the surface microlayer were 30% and 23%, respectively, of the amounts in the whole depth of subsurface water. Because the nature of the surface microlayer is profoundly affected by turbulence and the presence of both natural and anthropogenic surface-active material, however, concentrations of toxic substances in the surface microlayer are extremely variable with time. At best, the surface microlayer serves as an imperfect indicator of subsurface water contamination.

Table 5-4 shows the concentrations of methyltin species in the same subsurface waters as in Table 5-2. Anthropogenic sources of methyltin species are their use as poly(vinyl chloride) stabilizers, or as catalysts. Table 5-4 shows that high concentrations of methyltin species are generally found near chemical plants or in harbors with heavy shipping traffic. Atmospheric transport could be the reason for the presence of methyltin species in areas remote from industrial activity such as Plastic Lake and North Bay. The presence of methyltin species in rainwater (Braman and Tompkins 1979; Tugrul et al. 1983) lends support to such a pathway. Methyltin species could also result from biotic or abiotic methylation of either organotin species or naturally occurring tin (vide infra).

There are very few data on the occurrence of organotin compounds in sediment. Tables 5-5 and 5-6 show some concentrations of butyltin and methyltin species, respectively, in sediments. In general, butyltin species are more prominent in sediment than are methyltin species, perhaps because of their wider application. In addition to butyltin species, butylmethyltin species have been detected in the sediments of some harbors in Ontario (Maguire 1984), and could be the result of biologically mediated methylation of anthropogenically derived butyltin species or a chemical redistribution reaction between anthropogenically derived butyl- and methyltin species.

Table 5-3. Concentrations of butyltin species and total recoverable inorganic tin (TRIT) in unfiltered surface microlayer (from Maguire *et al*. 1982)[α].

Location	Concentration ($mol.L^{-1}$ Sn)		
	Bu_3SnQ	Bu_2SnQ_2	TRIT
Lake Superior (Thunder Bay)	1.6×10^{-9}		9.3×10^{-7}
Lake Superior (Red Rock)	2.3×10^{-9}	3.1×10^{-9}	3.5×10^{-7}
Lake Superior (Marathon)			9.8×10^{-8}
Turkey Lake 1	1.0×10^{-9}		6.8×10^{-7}
Turkey Lake 2	2.9×10^{-9}		3.6×10^{-6}
Turkey Lake 3	1.7×10^{-9}		2.3×10^{-7}
Turkey Lake 4	1.0×10^{-9}		3.6×10^{-7}
Turkey Lake 5	5.2×10^{-10}		7.0×10^{-7}
Sault Ste. Marie Harbour	1.0×10^{-9}		3.3×10^{-7}
Ramsey Lake (Sudbury)	8.6×10^{-10}		7.7×10^{-8}
Nepewassi Lake (Sudbury)	1.3×10^{-8}		4.2×10^{-6}
Lake Nipissing (North Bay)	6.2×10^{-10}		1.5×10^{-6}
Collingwood Harbour			2.6×10^{-6}
Owen Sound Harbour			1.8×10^{-6}
St. Clair River 1	2.1×10^{-7}	4.0×10^{-7}	7.1×10^{-8}
St. Clair River 2	4.1×10^{-8}	1.1×10^{-5}	2.6×10^{-7}
St. Clair River 3		9.4×10^{-6}	2.5×10^{-9}
Lake St. Clair (Mitchell Bay)	3.0×10^{-8}	5.1×10^{-7}	1.1×10^{-6}
Lake St. Clair (marina)	1.8×10^{-7}	4.6×10^{-7}	5.6×10^{-8}
Thames River (400 m upstream from mouth)			1.0×10^{-7}
Port Dover Harbour	4.1×10^{-8}	2.2×10^{-7}	2.1×10^{-8}
Grand River (mouth)			
Toronto Harbour		6.3×10^{-6}	4.8×10^{-7}
Whitby Harbour	4.8×10^{-9}	9.7×10^{-6}	5.3×10^{-6}
Belleville Harbour	1.9×10^{-7}	8.4×10^{-7}	6.7×10^{-7}
Kingston Harbour	1.7×10^{-8}	1.7×10^{-7}	3.9×10^{-7}
St. Lawrence River 1	3.3×10^{-8}	1.6×10^{-7}	1.2×10^{-8}
St. Lawrence River 2			6.7×10^{-9}

[α] Q is the counterion; $BuSnQ_3$ not detected in any surface microlayer sample; blank means not detected; the minimum detectable concentration of each species is approximately 3.4×10^{-11} $mol.L^{-1}$ Sn.

Table 5-4. Concentrations of methyltin species in lakes and rivers in Ontario (from Maguire *et al*. 1982)[α].

Location	Concentration (mol.L^{-1} Sn)		
	Me_3SnQ	Me_2SnQ_2	$MeSnQ_3$
Lake Superior (Thunder Bay)		2.5×10^{-10}	1.3×10^{-9}
Lake Superior (Red Rock)	4.2×10^{-10}	2.5×10^{-10}	1.9×10^{-9}
Lake Superior (Marathon)		2.5×10^{-10}	1.8×10^{-9}
Turkey Lake 1		4.2×10^{-10}	2.0×10^{-9}
Turkey Lake 2		1.7×10^{-10}	9.2×10^{-10}
Turkey Lake 3		4.2×10^{-10}	1.5×10^{-9}
Turkey Lake 4		3.4×10^{-10}	1.7×10^{-9}
Turkey Lake 5		4.2×10^{-10}	2.1×10^{-9}
Sault Ste. Marie Harbour		3.4×10^{-10}	2.1×10^{-9}
Ramsey Lake (Sudbury)		3.4×10^{-10}	1.9×10^{-9}
Nepewassi Lake (Sudbury)		2.5×10^{-10}	1.7×10^{-9}
Lake Nipissing (North Bay)		7.6×10^{-10}	1.9×10^{-9}
Plastic Lake		3.4×10^{-10}	1.4×10^{-9}
Collingwood Harbour		4.2×10^{-10}	1.7×10^{-9}
Owen Sound Harbour		3.4×10^{-10}	1.4×10^{-9}
St. Clair River 1		1.5×10^{-9}	5.4×10^{-9}
St. Clair River 2		1.8×10^{-9}	5.7×10^{-9}
Lake St. Clair (Mitchell Bay)		9.2×10^{-10}	2.9×10^{-9}
Lake St. Clair (marina)		1.9×10^{-9}	4.5×10^{-9}
Thames River (400 m upstream from mouth)		1.8×10^{-9}	5.6×10^{-9}
Port Dover Harbour		1.3×10^{-9}	5.1×10^{-9}
Grand River (mouth)		1.2×10^{-9}	3.1×10^{-9}
Hamilton Harbour			5.0×10^{-10}
Toronto Harbour		2.4×10^{-9}	8.1×10^{-9}
Whitby Harbour		2.4×10^{-9}	1.0×10^{-8}
Belleville Harbour		2.0×10^{-9}	7.7×10^{-9}
Kingston Harbour		3.4×10^{-9}	1.0×10^{-8}
St. Lawrence River 1		2.5×10^{-10}	2.4×10^{-9}

[α] Q is the counterion; blank means not detectable; the minimum detectable concentration of each species is approximately 1.68×10^{-10} mol.L^{-1} Sn.

Table 5-5. Concentrations of butyltin species and total recoverable inorganic tin (TRIT) in top 2 cm of sediment (from Maguire 1984)[α].

Location	Concentration ($mol.kg^{-1}$ (dry weight) Sn)			
	Bu_3SnQ	Bu_2SnQ_2	$BuSnQ_3$	TRIT
Lake Superior (Thunder Bay)				3.69×10^{-6}
Lake Superior (Red Rock)				3.36×10^{-6}
Turkey Lake 2				8.40×10^{-6}
Turkey Lake 3				4.97×10^{-6}
Turkey Lake 4				6.07×10^{-6}
Turkey Lake 5				4.38×10^{-6}
Sault Ste. Marie Harbour				1.46×10^{-5}
Nepewassi Lake (Sudbury)				1.75×10^{-6}
Lake Nipissing (North Bay)				5.76×10^{-6}
Plastic Lake				9.41×10^{-6}
Owen Sound Harbour				6.47×10^{-6}
Lake St. Clair (marina)	3.45×10^{-7}	3.15×10^{-7}	1.32×10^{-7}	9.58×10^{-7}
Port Dover Harbour	4.45×10^{-7}	2.78×10^{-7}	5.33×10^{-7}	2.64×10^{-6}
Grand River (mouth)	1.06×10^{-7}	3.85×10^{-8}	8.01×10^{-8}	1.98×10^{-6}
Toronto Harbour	1.86×10^{-6}	1.49×10^{-6}	3.29×10^{-6}	4.31×10^{-5}
Whitby Harbour	3.79×10^{-7}	2.05×10^{-7}	7.84×10^{-8}	1.10×10^{-6}
Belleville Harbour				1.22×10^{-5}
Kingston Harbour	1.41×10^{-6}	6.52×10^{-7}		1.34×10^{-5}
St. Lawrence River 1				4.86×10^{-6}
St. Lawrence River 2				6.89×10^{-7}

[α] Q is the counterion; blank means not detected; the minimum detectable concentration of each species is approximately 1.7×10^{-8} $mol.kg^{-1}$ (dry weight) Sn.

Table 5-6. Concentrations of methyltin species and inorganic tin in top 2 cm of sediment (from Chau *et al*. 1984)[a].

Location	Concentration (mol.kg^{-1} (dry weight) Sn)			
	Me_3SnQ	Me_2SnQ_2	$MeSnQ_3$	Sn(IV)
St. Lawrence River, East Montreal		4.55×10^{-7}		4.02×10^{-7}
St. Lawrence River, East Cornwall			2.65×10^{-7}	2.12×10^{-7}
Toronto Harbour		1.78×10^{-6}		6.80×10^{-6}
Lake Erie, West basin	9.58×10^{-7}			
Wabigoon River, upstream Clay Lake		1.11×10^{-6}		2.54×10^{-6}

[a] Q is the counterion; blank means not detected; the minimum detectable concentration of each species is approximately 8.4×10^{-8} mol.kg^{-1} (dry weight) Sn.

5.3 ORGANOTIN COMPOUNDS IN ESTUARINE AND MARINE WATERS

As well as there being an interest in naturally occurring methylated tin, there is considerable concern regarding the amounts of synthetic organotin compounds that may be entering the marine hydrosphere and their potential conversions to other species by biologically mediated reactions. One example of such a route is the widespread use of organotin antifouling paints which commonly contain the tributyltin moiety. Since the oceans are also the end points of river runoff, there is growing concern over the wide variety of industrial organotin chemicals that are discharged into rivers and their long-term effects on the biosphere. Only recently has the detection and quantification of low concentrations of organotin compounds in aqueous media been feasible. To date, no measurements have been made of organotin species in Canadian estuarine and marine waters.

Reports of methylated tin in seawater are still essentially synoptic in nature, with data reported for a considerable number of locations, primarily in the continental United States. There have been few attempts as yet, except perhaps for studies by Byrd and Andreae (1982), to investigate systematic changes in estuaries and coastal shelf waters.

The first report of methylated tin in seawater is attributed to Braman and Tompkins (1979) (see Appendix V.0). Samples from the Gulf of Mexico and Tampa Bay were in most cases found to contain measurable amounts of mono-, di- and trimethyltin species in the range of 3.7-22 pmol.L^{-1} (0.44-2.6 ng.L^{-1} Sn), with a slight dominance of the dimethyl form. As was the case for total inorganic tin, there were two or three notably high values which might be attributable to contamination during sampling. Estuarine samples contained similar but higher concentrations ranging from 1.9 to 63 pmol.L^{-1} (0.22-7.4 ng.L^{-1} Sn); the monomethyltin moiety was dominant. Hodge *et al.* (1979) found that only samples from San Diego Bay contained mono- and dimethyltin species in ranges of 15-60 pmol.L^{-1} (1.8-7.1 ng.L^{-1} Sn) and 101-302 pmol.L^{-1} (12-36 ng.L^{-1} Sn), respectively. No methyltin compounds were detected in "cleaner" San Francisco Bay and coastal California waters.

The highly contaminated (by urban and industrial runoff) waters of Baltimore Harbor were reported (Jackson *et al.* 1982; Brinckman *et al.* 1983) to contain di-, tri- and tetramethyltin moieties in quantities ranging from less than 34 pmol.L^{-1} to 1.7 x 10^{3} pmol.L^{-1} (4.0-200 ng.L^{-1} Sn) in surface and bottom waters. The monomethyl species was not detectable. These studies are of particular interest because of the discovery of $(CH_3)_4Sn$ and methyltin hydrides $(CH_3)_nSnH_{4-n}$ (n = 2,3), which were identified by sample purging before addition of the borohydride reductant. Quantities of all tin species varied greatly over the 3-week sampling period.

Estuarine profiles of $(CH_3)_2Sn^{2+}$ species (Figure 5-1) were reported by Byrd and Andreae (1982). Concentrations increased with

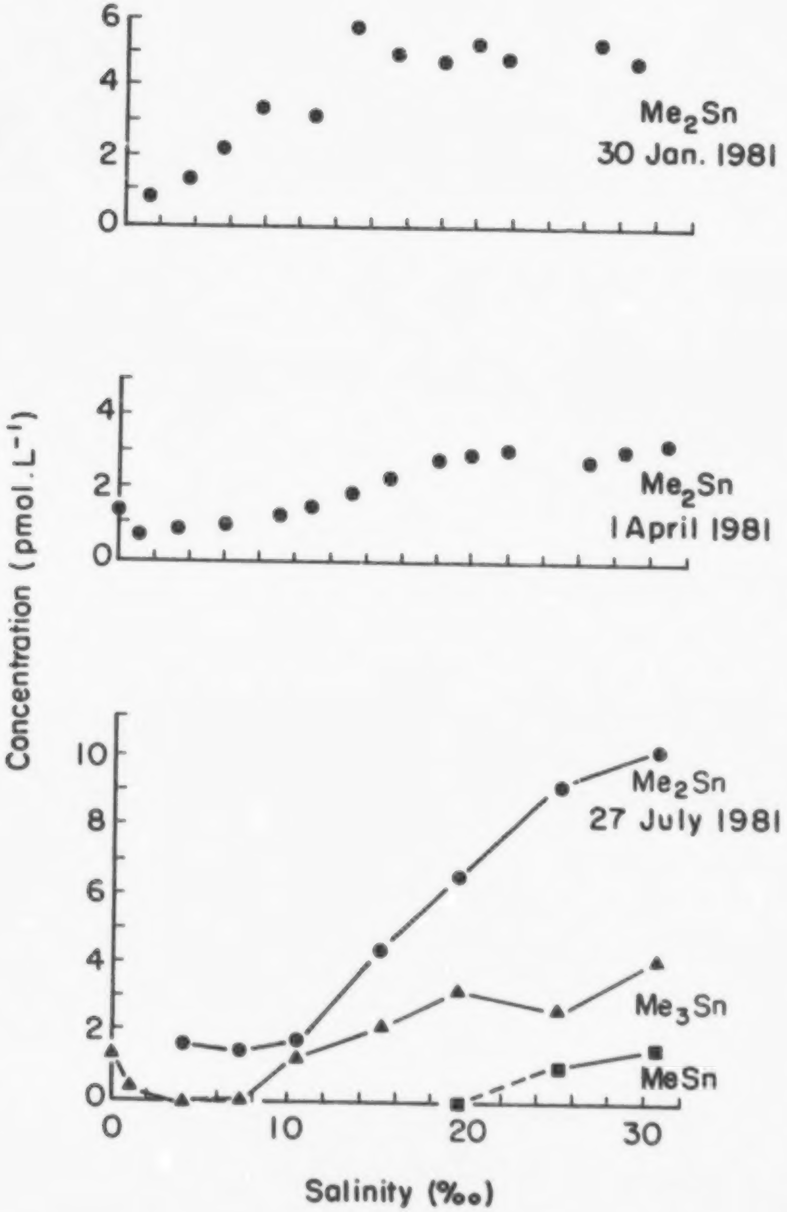


Figure 5-1. Profiles of methyltin species in the Ochlockonee River estuary (from Byrd and Andreae 1982).

salinity in the Ochlockonee River estuary (Florida), indicating production of this species. However, it was not clear whether this was due to production in the water column or to input from the sediments. Concentrations of $(CH_3)_2Sn^{2+}$ species on two sampling dates were no greater than 6 pmol.L^{-1} (0.7 ng.L^{-1} Sn). However, during a third sampling at low tide, concentrations of $(CH_3)_2Sn^{2+}$ species were ≈10 pmol.L^{-1} (1.2 ng.L^{-1} Sn) with quantities of $(CH_3)_3Sn^+$ and CH_3Sn^{3+} species also found. On this date the sum of methyltin species in the saline end-member exceeded inorganic tin by a factor of 2.

Only mono- and dimethyltin moieties were measured by Tugrul et al. (1983) in harbor waters at three locations on the Turkish coast. The highest total inorganic tin concentrations (Appendix V.0) were matched by concomitantly high values of the methyl species ranging from 134 to 313 pmol.L^{-1} (15.8-36.9 ng.L^{-1} Sn).

To date there have been three reports of butyltin species in saline waters. Jackson et al. (1982) and Brinckman et al. (1983) described the finding of the volatile hydride $C_4H_9SnH_3$ and the aquated ion $C_4H_9Sn^{3+}$ in Baltimore Harbor waters. Concentrations ranged from 280 to 1.7 x 10^3 pmol.L^{-1} (33-200 ng.L^{-1} Sn). The presence of these species is probably due to release from antifoulants. More recently, Andreae et al. (1983) reported the discovery of significant amounts of the monobutyltin moiety in waters of the Tejo River estuary, Portugal, where antifoulants were also implicated.

No other organotin species (e.g. phenyl, cyclohexyl) have been reported thus far. However, their discovery may await improved sampling and analytical methods.

Clearly, additional data for world coastal areas and the open oceans are required. While the data currently available provide ranges of values, there is a need for support of these figures using alternative methodologies that eliminate the possibility of rearrangement of methyl groups which may occur in hydride evolution. Little attention has been paid thus far to potential contamination and to quality control which is very essential at the picomolar levels involved. As is now well recognized with other trace metal studies that are considered to be at a more advanced stage of development, the greatest of care must be taken at all stages of the study, particularly at the sampling point.

5.4 PERSISTENCE AND FATE IN AQUATIC SYSTEMS

The persistence and fate of any toxic substance in any environmental "compartment" is a function of the kinetics of a variety of routes of degradation and dissipation. In aquatic systems, some of the more important considerations, in addition to simple water flow, are basic properties such as aqueous solubility and vapor pressure, and such processes as hydrolysis (or stability in the dark), volatilization, sunlight photolysis, adsorption to suspended matter and to sediments, and abiotic and biotic methylation and demethylation. Uptake and degradation of organotin compounds by aquatic organisms will be discussed in Section 5.5.

Before the literature is reviewed, there are a few points to note:

(i) The persistence of any organotin compound should not be defined in terms of the time required for anion exchange; that gives a false impression of degradation kinetics when what is significant is a definition in terms of loss of alkyl or aryl groups, since the toxicity of organotin compounds to most organisms decreases with decreasing number of organic substituents at the tin atom, in the series of tri-, di-, and monosubstitution (Davies and Smith 1980).

(ii) The persistence of any toxic substance in a water-sediment system should not be defined solely in terms of adsorption to sediment, since toxic residues could be mobilized again through sediment re-suspension, or could be taken up by benthic biota.

(iii) Although the use of Hg lamps in the laboratory yields much useful information on chemical mechanisms, the use of environmentally more relevant light sources (i.e. sunlight or appropriately filtered light of suitable intensity) will yield more reliable estimates for persistence with regard to sunlight photolysis.

(iv) Some organotin species, and inorganic tin, adsorb to Teflon and glass under certain conditions (Meinema _et al_. 1978; Maguire _et al_. 1983); such adsorption may vitiate the findings of some workers.

Appendix VII.0 contains detailed information on the properties and transformations of inorganic tin and organotin compounds that are relevant to their aquatic environmental fate. Some information on biological transformations other than biomethylation is included; these will be discussed in more detail in Section 5.5.

5.4.1 ABIOTIC DEGRADATION

For convenience, the discussion on the persistence and fate of tin and organotin compounds will treat the compounds separately by class, as they are found in Appendix VII.0.

The Sn^{4+} oxidation state is thermodynamically more stable than Sn^{2+} (Cotton and Wilkinson 1962) and thus in most environmental compartments, with the exception of some anaerobic sediments, inorganic tin will likely be found in the Sn^{4+} state. Brinckman _et al_. (1983) suggested that some Sn(II) species may also exist, especially in waters with lower redox potentials. At present, borohydride reduction methods do not differentiate between the two oxidation states. Fanchiang and

Wood (1981) have shown that the half-life for oxidation of Sn^{2+} to Sn^{4+} is about 2 d in oxygenated water at 23°C.

Since Sn(IV) does not exist as the free aquated cation Sn^{4+}, the most likely forms of the element in natural waters are the hydroxide $Sn(OH)_4$, or the hydroxyoxides $SnO(OH)_2$ and $SnO(OH)_3$. Speciation is dependent on pE and pH. At a pH of 8 or above in waters with normal levels of oxygen it is suggested (Stumm and Brauner 1975) that $SnO(OH)_3$ is the predominant species. Anodic stripping studies (Macchi and Pettine 1980) indicated that the neutral $SnO(OH)_2$ should predominate at pH levels less than 7. Controlled ecosystem experiments (Amdurer et al. 1983) employing a ^{113}Sn tracer and a selective column separation technique, however, provide contradictory evidence that points to $SnO(OH)_2$ as the major inorganic form in seawater.

In order to understand the environmental fate of organotin compounds, it is important to know their chemical speciation in natural waters and sediment. Very little work has been performed in this area to date. Triorganotin hydroxides or bis oxides appear to react with ions in seawater to form an equilibrium mixture of the starting material, the chloride, the carbonate and the "aquo complex", the relative amounts being a function of pH (Guard et al. 1982; Laughlin 1984). In general, it is expected that minimal concentrations of the cation would be present except in fresh waters with low pH (Laughlin 1984). Extensive work is required to determine the nature of solvated organotin compounds in natural waters at relevant environmental concentrations.

Aside from the potential for biomethylation (see Section 5.4.2), methyltin compounds can also be sequentially demethylated to inorganic tin by photolysis; however, an estimate of an "environmental half-life" is uncertain since light of wavelengths less than 290 nm (the lower limit for sunlight) was used. Estimated lower limits for these photolytic half-lives in water are 30 h for $(CH_3)_3Sn^+$, 300 h for $(CH_3)_2Sn^{2+}$ and 1500 h for CH_3Sn^{3+} (Blunden 1983).

Neat $(CH_3)_3SnOH$ (and the bis oxide) will react with atmospheric CO_2 to produce $((CH_3)_3Sn)_2CO_3$ (Brown et al. 1972); however, in water, $(CH_3)_3Sn^+$ will probably remain as the hydrated cation in the presence of dissolved CO_2. This comment is applicable to all neat trialkyltin hydroxides or bis(trialkyltin) oxides that react with atmospheric CO_2 to yield carbonates.

Little reliable information is available on the environmental persistence or fate of ethyl-, propyl-, pentyl-, hexyl-, octyl- and mixed cyclohexylphenyltin compounds. These six classes of organotin compounds are either little used or are not very toxic to most organisms.

The literature on butyltin compounds is, in contrast, fairly extensive. The tributyltin species does not lose butyl groups in the dark, and does not volatilize over a period of at least 2 months (Maguire et al. 1983). There is evidence for its strong binding to soils and sediment, the formation of residues that are not extractable (Sheldon 1978) and microbial dealkylation (Barug and Vonk 1980). Soil-bound $(C_4H_9)_3Sn^+$ should not be considered biologically unavailable; Gile et al. (1982) have presented some equivocal evidence for its uptake by earthworms.

Estimates of the photolytic half-life of the $(C_4H_9)_3Sn^+$ species in sunlight have been given as 18 d (Slesinger and Dressler 1978) and >89 d (Maguire et al. 1983). This discrepancy may have been the result of different kinds and concentrations of naturally occurring photosensitizers. Recoveries of products of $(C_4H_9)_3Sn^+$ photolysis were generally poor. One reason for this, by analogy with phenyltin compounds (Soderquist and Crosby 1980), may be that water-soluble, nonextractable, polymeric di- and monobutyltin species were formed.

Maguire (1984) reported the occurrence of methylated derivatives of $(C_4H_9)_3Sn^+$ and $(C_4H_9)_2Sn^{2+}$ species in a few harbor sediments. Their concentrations relative to the parent species suggested that methylation may be a significant pathway of transformation of butyltin species in sediment-water mixtures.

The $(C_4H_9)_3Sn^+$ species appears to be at least moderately persistent in aquatic ecosystems. Adsorption to sediments may be an important pathway, but the strength of adsorption and the biological availability of sediment-associated $(C_4H_9)_3Sn^+$ require further attention.

There are fewer data on $(C_4H_9)_2Sn^{2+}$ and $C_4H_9Sn^{3+}$; photolytic half-lives are generally of the same order as those for $(C_4H_9)_3Sn^+$.

Photolysis of tricyclohexyltin on surfaces proceeds with an estimated "sunlight half-life" of 8 d (Smith et al. 1976), and appears to proceed through sequential dealkylation. Volatilization from water is at least 10 times slower. There is some evidence for strong binding to soil and dealkylation by soil microbes (Blair 1975). Photolysis in water produces cyclohexane and cyclohexanol (Smith et al. 1976), indicating dealkylation, but half-lives are not available. The above statements are generally applicable to $(C_6H_{11})_2Sn^{2+}$ and $C_6H_{11}Sn^{3+}$.

The triphenyltin species appears to bind strongly to soil as evidenced by a 50% decrease in extractability over 40 d (Barnes et al. 1973). Sunlight photolysis on surfaces ($t_{\frac{1}{2}} \approx 14$ d) and in water ($t_{\frac{1}{2}}$ is 14-21 d) appears to proceed through sequential dearylation, although there is evidence for formation of water-soluble polymeric di- and monophenyltin species (Soderquist and Crosby 1980). The $(C_6H_5)_3Sn^+$ species is stable in water in the dark for over a month, and is slowly degraded ($t_{\frac{1}{2}} \approx 140$ d) by microbes in soil (Barnes et al. 1973). At low concentrations, $(C_6H_5)_2Sn^{2+}$ and $C_6H_5Sn^{3+}$ are much less stable in water

($t_{\frac{1}{2}}$ is several minutes for $C_6H_5Sn^{3+}$ and <3 d for $(C_6H_5)_2Sn^{2+}$), and there is evidence for the rapid formation of water-soluble polymeric tin species (Soderquist and Crosby 1980). Triphenyltin chloride on sugar beet leaves degraded to inorganic tin, apparently by sequential destannylation through the di- and monophenyltin compounds. However, a dark control was not reported and no degradation was noted in stems or roots (Freitag and Bock 1974b).

In general, studies on the persistence of the major classes of organotin compounds indicate that abiotic degradation generally occurs, as does biological degradation, through mechanisms of sequential dealkylation or dearylation. Adsorption to soils and sediments appears to be strong, although subsequent mobilization by biota cannot be ruled out. Photolysis may be the rate-limiting chemical degradation pathway.

5.4.2 METHYLATION/DEMETHYLATION

Of particular concern as substrates for methylation in the environment are compounds used in industrial processes and as biocides. These include inorganic tin compounds, mono-, di-, and tributyltin species, dioctyltin, triphenyltin and tricyclohexyltin compounds, and potential degradation products of some of these compounds (Craig 1980). Biological and chemical aspects of biomethylation have been reviewed (Wood 1974; Ridley et al. 1977; Brinckman and Bellama 1978; Craig 1980; Brinckman 1981; Thayer and Brinckman 1982; Thayer 1984). The methylation of inorganic tin and methyltin compounds should not be discounted as a significant environmental phenomenon, since the process can convert tin (i) to more volatile forms capable of atmospheric distribution, and (ii) to more toxic forms.

Brinckman, Iverson and colleagues reported that a Pseudomonas sp. isolated from estuarine sediments could form methyltin compounds from inorganic Sn(II) or Sn(IV). They proposed that, in the presence of methyltin species, Hg(II) reacted to yield methylmercuric ion. Thus, biological methylation of tin contributed to formation of methylmercury (Huey et al. 1974; Brinckman and Iverson 1975; Brinckman et al. 1983). However, full identification of the product species was not achieved and biological methylation was not considered proven (Craig 1980).

Since then, several workers have shown that Sn^{4+} and methyltin compounds can be methylated in nutrient medium or natural water-sediment mixtures. CH_3Sn^{3+}, $(CH_3)_2Sn^{2+}$, $(CH_3)_3Sn^+$, $(CH_3)_4Sn$ and a methyltin hydride of unknown composition (but more volatile than $(CH_3)_4Sn$) have been variously identified as products. Guard et al. (1981) incubated oxygen-deficient sediments from San Francisco Bay with trimethyltin hydroxide, apparently under aerobic conditions. They detected production of tetramethyltin in "biologically active" (nonautoclaved) flasks and in autoclaved controls. Nonautoclaved flasks contained 2.7 times more tetramethyltin than did autoclaved flasks. The production of tetramethyltin in nonautoclaved flasks was enhanced by added sulfide or acetate. Over a 80-d incubation period, 2.4% of the trimethyltin hydroxide added was detected in the headspace gas. The data support the existence of both biotic and abiotic pathways for the formation of tetramethyltin, and the authors suggested that the environmental significance of the transformation of trimethyltin to tetramethyltin is minor. Chau et al. (1981) used sediments from Canadian Shield lakes in Ontario to demonstrate that sediments incubated in a microbiological medium containing tin could methylate the tin. The transformation of methyltin(IV) compounds occurred more readily than that of inorganic Sn(II) or Sn(IV).

Dimethyltin and trimethyltin compounds were detected by GC and by GC-MS after 14 d of aerobic incubation in nutrient medium containing $SnCl_4$ inoculated with sediment from Chesapeake Bay. Methylated tin species were not observed in sterile controls or in poisoned controls (Cooney et al. 1981; Hallas et al. 1982a).

In addition to mixed cultures from sediments, pure cultures can effect methylation. Brinckman and colleagues (Blair et al. 1981; Brinckman 1981; Jackson et al. 1982) have provided GC-MS data to demonstrate that pure cultures of a Pseudomonas growing on a laboratory medium can transform Sn(IV) and, to a lesser extent, Sn(II) to trimethyltin species. Dimethyl- and trimethylstannanes were also detected, and less compelling evidence was obtained for the production of tetramethyltin. Di-, tri- and tetramethylstannanes were also found in samples of water from Chesapeake Bay and Baltimore Harbor. In addition, Seidel et al. (1980) incubated unidentified bacteria obtained from seaweed samples in synthetic seawater medium containing inorganic Sn(IV) and observed the production of tetramethyltin, which was identified by its GC retention time. Thus, a number of the reactions in the "tin cycle" proposed by Ridley et al. (1977) have been demonstrated to occur in laboratory experiments.

Tributylmethyltin and dibutyldimethyltin were found in sediments from several harbors in Canada, suggesting that some butyltin species can be methylated in aquatic environments (Maguire 1984).

From a survey of rivers in Germany and in the southeastern U.S., Byrd and Andreae (1982) found that mono-, di- and trimethyltin compounds were almost ubiquitous, but dimethyltin compounds predominated. They concluded that among the natural inputs to these systems, biomethylation was the major source. Anthropogenic sources, including industrial use of dialkyltin compounds as PVC stabilizers, could also be contributing factors.

Biological methylation of tin may be dependent on methyl transfer from methyl cobalamin (methyl-B_{12}). Other methylating species, S-adenosyl methionine and N-5-methyltetrahydrofolate, are not regarded as being able to transfer methyl to positively charged metals (Ridley et al. 1977; Wood et al. 1978). Kinetic and mechanistic studies involving methyl-B_{12} were discussed by Fanchiang et al. (1978). It was suggested that reductive cleavage of the Co-C bond involves a transient Sn(III) radical which is generated by oxidation of Sn(II) (Ridley et al. 1977; Dizikes et al. 1978). $SnCl_2$ reacted aerobically with methyl-B_{12}, ethyl-B_{12}, or chloromethyl-B_{12} to yield methyltin(IV) trichloride (Fanchiang and Wood 1981). The reaction did not occur under anaerobic conditions, suggesting that it would not occur in oxygen-deficient sediments. Halide ions decreased the rates of reaction of other heavy metals with methyl-B_{12} (Blum and Bartha 1980; Thayer 1981) and presumably would affect the reaction with tin. This may be significant in estuarine and marine ecosystems.

Presumably, similar mechanisms operate in subsequent methylations to yield di-, tri- and tetramethyltin compounds, but evidence is not available to support those mechanisms.

Transmethylation reactions involving methyl-B_{12} can take place abiotically (Thayer 1979). Thus, methyl-B_{12} secreted by living cells or released by dead cells, or cobalamin from an abiotic source could be involved. Brinckman et al. (1983) noted the high concentrations (1.9-27.1 $\mu g.g^{-1}$) of cobalamins (vitamin B_{12} derivatives) that occur in activated sludge sewage treatment systems, and suggested that CH_3-B_{12} might be involved in the methylation of tin and other metals during sewage treatment. Since cobalamins are sensitive to light, microbe-mediated, extracellular, or nonbiological methylations would be expected to be limited in niches that receive bright sunlight.

Seidel et al. (1980) pointed out that activities such as the methylation of tin reported for macroalgae could be due to epibiotic bacteria present on the algae. Brinckman et al. (1983) noted that the adsorption and concentration of tin and microorganisms on suspended particulates and in surface slicks could provide sites for biomethylation in aquatic ecosystems.

Craig (1980) and Craig and Rapsomanikis (1981) pointed out limitations for reactions between metals and methyl-B_{12} under normal conditions and recommended a search for additional pathways. Alternative, abiotic mechanisms for the methylation/demethylation of tin, including generation of di-, tri- and tetramethyltin compounds, are discussed in Section 5.4.1. Abiotic formation of methyltin triiodide by the reaction of tin sulfide and methyl iodide in water has been observed (Manders et al. 1984).

Ridley et al. (1977) proposed that sequential demethylation of tetramethyltin to tri-, di- and monomethyltin compounds, and eventually to inorganic Sn(IV), occurs and is mediated by mixed function oxidases as in rat liver microsomes (Kimmel et al. 1977).

In summary, methylation and demethylation reactions are likely to occur in aquatic ecosystems by both biological and abiotic mechanisms. The relative contributions of various mechanisms, the rates in situ, and the importance of these reactions in nature remain to be determined.

5.5 DISTRIBUTION AND DEGRADATION IN AQUATIC BIOTA

5.5.1 ANIMALS

5.5.1.1 Introduction

Several investigators have measured concentrations of inorganic tin in aquatic organisms (see, for example, Smith 1970; Smith and Burton 1972; Braman and Tompkins 1979; Hodge et al. 1979; Seidel et al. 1980; Dogan and Haerdi 1980; Maher 1982). Few workers, however, have examined the accumulation of organotin compounds by aquatic biota.

The question of bioaccumulation and food chain biomagnification of any toxic chemical is obviously an important one. The tendency of a chemical to be concentrated by an organism depends on the compound's partition behavior between the lipid and aqueous phases, which is reflected by its octanol-water partition coefficient. In general, the larger the number and molecular weight of organic groups attached to the tin atom, the lower the compound's solubility in water and the higher its solubility in octanol (Selwyn 1976; Zuckerman et al. 1978; Wong et al. 1982). The octanol-water partition coefficients for several organotin compounds (Table 5-7) suggest that the potential for bioaccumulation exists, particularly for those compounds whose R groups are at least as large as the butyl group. The work of Laughlin et al. (1984a) suggests that the aqueous solvation free energy of triorganotin compounds governs their uptake; larger organotin molecules would have greater interactions with the aqueous solvent and hence would cause larger free energy changes when partitioning into lipids (the rate-limiting step being diffusion into the organism's lipid pool). As Laughlin et al. (1984a) point out, however, the uptake of organotin compounds much larger than the tricyclohexyltin species will probably be reduced by limited diffusivity into lipids in spite of decreased aqueous activity.

The following sections will review the information that exists on the uptake, distribution, metabolism and elimination of organotin compounds by aquatic invertebrate and vertebrate organisms.

5.5.1.2 Uptake and Distribution

Most studies of the uptake and distribution of organotin compounds in fish have been conducted by Russian researchers on the carp, Cyprinus carpio. In experiments using radioactively labelled (^{117}Sn) triethyltin chloride (Stroganov et al. 1973; Filenko and Parina 1981), the relatively high content of radioactive tin (assumed to represent the triethyltin moiety) in the esophagus and gut (Table 5-8) indicated that some of the compound entered the body of the fish through the digestive tract before being absorbed into the bloodstream. The skin, on the other hand, appeared to be poorly permeable to low concentrations of the triethyltin compound; the lipids contained in the

Table 5-7. Octanol-water partition coefficients (K_{ow}) and predicted bioconcentration factors (BCF) for several organotin compounds.

Compound	log K_{ow}	BCF[α]	Reference
Trimethyltin chloride	-2.9	6.3×10^{-4}	Wulf and Byington (1975)
Triethyltin bromide	0.57	0.60	"
Tripropyltin chloride	1.7	5.6	"
Tributyltin chloride	3.1	79	"
Tributyltin fluoride	3.2	100	U.S. EPA (1979), cited by Jones and Millson (1982)
Bis(tributyltin) oxide	3.3	125	"
Tributyltin species	3.7-3.8[β]	280-340	Laughlin (1984)
Triphenyltin fluoride	3.4	160	U.S. EPA (1979), cited by Jones and Millson (1982)
Triphenyltin chloride	4.1	630	Wulf and Byington (1975)
Tricyclohexyltin hydroxide	4.3	1000	"

[α] The bioconcentration factor, BCF, is calculated from the following equation:

$$\log \mathrm{BCF} = -0.70 + 0.85 \log K_{ow}$$

which was developed by Veith *et al*. (1979) for several fish species (fathead minnow (*Pimephales promelas*), bluegill (*Lepomis macrochirus*), mosquitofish (*Gambusia affinis*), rainbow trout (*Salmo gairdneri*) and green sunfish (*Lepomis* sp.)). Other regression equations that may be used to estimate bioconcentration factors from partition coefficients can be found in Table 8-1 of Roberts *et al*. (1981).

[β] Value varies as a function of salinity.

Table 5-8. Distribution of triethyltin species in organs and tissues of carp as a function of time and concentration of radioactively labelled triethyltin chloride in the water (adapted from Stroganov *et al*. 1973).

Organ, tissue or fluid	Concentration of triethyltin species (nmol.g^{-1} dry weight unless otherwise indicated) at following exposure times and concentrations of triethyltin chloride in water							
	1 mg.L^{-1} (4 µmol.L^{-1} Sn)		0.1 mg.L^{-1} (0.4 µmol.L^{-1} Sn)			0.01 mg.L^{-1} (0.04 µmol.L^{-1} Sn)		
	2 d	6 d	15 d	30 d	45 d	15 d	30 d	45 d
Liver	3.9	3.4	2.0$^{\alpha}$	3.6$^{\alpha}$	4.1$^{\alpha}$	0.8$^{\alpha}$	1.0$^{\alpha}$	1.2$^{\alpha}$
Brain	6.3	3.4	1.3$^{\alpha}$	2.6$^{\alpha}$	3.5$^{\alpha}$	0.7$^{\alpha}$	1.3$^{\alpha}$	1.9$^{\alpha}$
Kidney	7.1	4.3	2.5$^{\alpha}$	3.1$^{\alpha}$	3.6$^{\alpha}$	0.5$^{\alpha}$	0.6$^{\alpha}$	0.8$^{\alpha}$
Spleen	5.5	3.6	0.9$^{\alpha}$	1.2$^{\alpha}$	1.2$^{\alpha}$	0.3$^{\alpha}$	0.5$^{\alpha}$	1.0$^{\alpha}$
Esophagus	6.2	11	1.3	3.2	4.6	0.41	0.82	1.3
Gut	4.7	8.9	3.7	11	19	1.7	14	4.3
Gills	3.8	6.2	0.90	1.9	3.5	0.45	0.53	0.70
Skin	20	5.9	0.49	0.62	1.4	0	0.25	0.57
Red muscles	3.9	2.6	1.0$^{\alpha}$	2.2$^{\alpha}$	2.6$^{\alpha}$	0.6$^{\alpha}$	1.2$^{\alpha}$	1.7$^{\alpha}$
White muscles	1.3	0.82	0.3$^{\alpha}$	0.5$^{\alpha}$	0.7$^{\alpha}$	0.1$^{\alpha}$	0.2$^{\alpha}$	0.3$^{\alpha}$
Gall bladder	53	350	170	250	290	7.6	27	34
Blood	24	18	3.8$^{\alpha}$	8.5$^{\alpha}$	9.0$^{\alpha}$	1.6$^{\alpha}$	3.4$^{\alpha}$	3.9$^{\alpha}$

Note: Concentrations of triethyltin species are calculated from measured radioactivity of ^{117}Sn.

$^{\alpha}$ Wet weight.

skin's mucous apparatus probably bound much of the chemical. The shortest route of entry of triethyltin species into the blood from the water appeared to be through the highly developed gill apparatus (Stroganov et al. 1973); an increase in the content of trimethyltin residues in gill tissues of carp exposed to 0.1 mg.L^{-1} labelled trimethyltin chloride (0.4 µmol.L^{-1} Sn) has also been observed (Parina et al. 1979).

After penetrating into the fish from the surrounding medium, organotin compounds enter the bloodstream. The blood of carp was found to accumulate the triethyltin moiety, and the amount depended on the external concentration and exposure time (Stroganov et al. 1973) (Table 5-8); the erythrocytes showed greater affinity for the compound than the blood plasma.

From the bloodstream, organotin toxicants are transported to various tissues of the carp. In general, the amounts of organotin compounds in the organs and tissues of carp were found to increase with duration of exposure and concentration of external medium (Stroganov et al. 1973; Parina et al. 1979; Filenko and Parina 1981). With fish exposed to 0.1 mg.L^{-1} labelled triethyltin chloride (0.4 µmol.L^{-1} Sn) for 45 d, for example, the amount of ^{117}Sn in the organs and isolated fractions was similar to that in carp kept 2 d in solution at a 10-fold higher concentration of triethyltin chloride (Stroganov et al. 1973) (Table 5-8). Parina et al. (1979) noted a general tendency for the content of radioactive label in carp tissues exposed to 1 mg.L^{-1} (4 µmol.L^{-1} Sn) labelled trimethyltin chloride to increase between day 7 and day 15; in chronic exposures to 0.1-0.01 mg.L^{-1} (0.04-0.4 µmol.L^{-1} Sn) for up to 45 d, the content in the organs and tissues rose proportionally with time up to 30 d.

The distribution of organotin compounds in individual carp tissues also appears to change with time; Stroganov et al. (1973) found that the triethyltin moiety (represented by ^{117}Sn) accumulated slowly at first in the backbone and scales, compared with soft tissues, then increased more rapidly because of the higher rate of metabolic processes in soft tissues and the low rate of exchange of mineral compounds in the skeleton of fishes. In general, the relative distributions of organotin compounds among individual organs and tissues of the carp depend on the tissue/blood distribution coefficients for the fish (Filenko and Parina 1981). Parina et al. (1979) found that carp exposed to labelled trimethyltin chloride accumulated the greatest quantities of radioactive label in bile and blood and the least amounts in bone and muscle tissue. Filenko and Parina (1981) observed that ^{113}Sn from labelled triethyltin and tripropyltin chloride was transferred most actively from the blood to the tissues of the brain and red muscles, and least actively to the liver and white muscles. These authors (Filenko and Parina 1982) suggest that the accumulation of trialkyltin species in brain tissue of carp following exposure plays a lead role in causing adverse effects on the fish. Stroganov et al. (1973) found the largest concentrations in the gall bladder (10-100 times more than in soft tissues and 100-1000 times more than in the external solution), presumably because of the liver's function of eliminating toxic substances entering the bloodstream by excreting them into the bile, which is then stored by the gall bladder. The authors suggested that significant amounts of the tin label found in the kidneys and spleen (Table 5-8) indicated that exposure to triethyltin chloride may affect the hematopoietic organs of the carp. Putintsev and Gameza (1980) observed that the radioactive tin label from trimethyltin chloride quickly accumulated in the hepatopancreas of carp before being detoxified and removed by the gall bladder.

The accumulation of triethyltin species (as indicated by ^{117}Sn content) in the organic constituents of the carp's liver, brain, and muscle tissue was determined by Stroganov et al. (1973). Accumulation was maximal in the glycogen of liver. The tissues of the brain and spinal cord had a high tendency to accumulate the triethyltin compound, the largest amounts being found in the lipid and glycogen fractions, which could lead to changes in the fish's fat and carbohydrate metabolism. Red muscles accumulated more triethyltin compound than white, possibly because of the significant lipid content in red muscles which would favor rapid binding of the triethyltin moiety to the tissue. Protein did not accumulate the compound to any great extent in any of the tissues examined.

There have been few studies of the uptake and distribution of organotin compounds by fish other than carp. Ward et al. (1981) examined the accumulation of bis(tributyltin) oxide by sheepshead minnows (*Cyprinodon variegatus*). After a 58-d exposure to 1.6 $\mu g.L^{-1}$ (mean) ^{14}C-labelled bis(tributyltin) oxide (5.4 $nmol.L^{-1}$ Sn), equilibrium between concentrations of the organotin compound in seawater and in the fish tissues was not reached. The measured tin concentrations in muscle, head and visceral portions of exposed sheepshead minnows increased steadily during the exposure period. The maximum observed bioconcentration factors were: x1810, muscle; x2120, head; x4580, viscera; x2600, whole fish. Bioconcentration was confirmed in various organs (especially liver) of fish exposed for 167 d to labelled bis(tributyltin) oxide and in 28-day-old juveniles, and was shown to increase with increasing concentrations of the organotin compound (see Table 5-9, Section 5.5.1.3).

It is important to note that these observed bioconcentration factors are up to 40 times higher than that predicted for bis(tributyltin) oxide on the basis of measured octanol-water partition coefficients (see Table 5-7, Section 5.5.1.1). These differences, if real, could indicate significant accumulation due to nonpartitioning mechanisms; on the other hand, the discrepancy could be attributed to incorrectly determined K_{ow} values (Laughlin 1984).

Leeuwangh et al. (1976) found that several species of fish, as well as the common pond snail (*Lymnaea stagnalis*), that were exposed to triphenyltin chloride accumulated tin up to a constant residue level, then died. The tin residues were determined by flameless atomic absorption spectrometry. The lethal total body residue level was species-dependent; the value of 14 µmol.kg^{-1} Sn for the roach (*Rutilus rutilus*) can be compared with the residue levels of tin (determined by neutron-activation analysis) in field tests of roach (1.6-3.8 µmol.kg^{-1} Sn), perch (2.5-5.3 µmol.kg^{-1} Sn) and pike (2.8 µmol.kg^{-1} Sn). Several organs and tissues of the goldfish (*Carassius auratus*) were analyzed by Leeuwangh *et al.* (1976), and showed *maximal* accumulation of tin in the brain and *minimal* accumulation in the muscles.

Evans and Laughlin (1984) showed that ingested food (in the form of brine shrimp (*Artemia salina*) labelled with ^{14}C-labelled bis(tributyltin) oxide) *provides a more* important route of uptake of bis(tributyltin) oxide by adults of the mud crab, *Rhithropanopeus harrisii*, than does direct uptake in water. In addition, the tissue distributions of the organotin compound accumulated from the two sources differed in that bis(tributyltin) oxide derived from food was transported more rapidly to internal organs. The hepatopancreas attained the highest concentration factor (4400) after 4 d; other tissues (including gills, carapace and testes) had concentration factors ranging from 500 to 1300. Because there was no indication that a steady state equilibrium had been reached, and because the absolute concentration of bis(tributyltin) oxide in the hepatopancreas was the same as that in the *Artemia* which they were fed, the authors suggested the possibility of biomagnification of bis(tributyltin) oxide concentration to higher levels than in food.

Waldock and Thain (1983) found bioconcentration factors of approximately 3000 and 10 000 for oysters (*Crassostrea gigas*) exposed to 1.6 and 0.15 µg.L^{-1} bis(tributyltin) oxide (5.4 and 0.51 nmol.L^{-1} Sn), respectively. Tributyltin concentrations in water and spat were determined using flameless atomic absorption spectrometry following acid/solvent extraction. Similarly, Waldock and Miller (1983) estimated a bioconcentration of 10 000-fold for *C. gigas* and 2000-fold for *Ostrea edulis* (European flat oyster) following exposure to the level of 0.15 µg.L^{-1} tributyltin species commonly found at one site in the United Kingdom. Subsequent experiments in which *C. gigas* and *O. edulis* were exposed to 0.15 µg.L^{-1} bis(tributyltin) oxide (0.51 nmol.L^{-1} Sn) for 21 d produced bioconcentration values of 6000-fold and 1500-fold, respectively (Waldock *et al.* 1983). The tissue concentrations of tributyltin compounds, determined by flameless atomic absorption spectrometry, indicated that *C. gigas* accumulated the organotin compound more rapidly and to a higher plateau concentration than did *O. edulis*.

Alzieu *et al.* (1982) observed that the tin concentrations in *Crassostrea gigas* in a harbor polluted by organotin compounds from antifouling paints were very high, reaching maximal values of tin of 0.93 mmol.kg^{-1} dried tissue (110 mg.kg^{-1}) by the end of the boating season. The total tin content of the tissues was determined by atomic absorption spectrometry using an electrothermal furnace. Tin levels in oyster gonads have also been found to be higher than normal in certain areas (Alzieu *et al*. 1980). Although the species of organotin compounds present or *their* concentrations were not identified, the authors compared their results with those of Ward *et al*. (1981), and concluded that oysters accumulate organotin compounds *more* readily than do fish, since fish exposed to 1.6 µg.L^{-1} ^{14}C-labelled bis(tributyltin) oxide (1.9 nmol.L^{-1} Sn) for 58 d accumulated only 13 µmol.kg^{-1} Sn. Young *et al*. (1979) noted that tin concentrations in mussel tissues were higher inside harbor areas, but did not determine whether the tin was present in organic or inorganic forms.

The accumulation of ^{14}C-labelled bis(tributyltin) oxide in the tissues and subcellular components of the adult snail, *Biomphalaria glabrata*, was examined by Allen *et al*. (1980). The initial absence of ^{14}C-label in the digestive system and high levels of the label in the head-foot tissue indicated that bis(tributyltin) oxide did not enter the snail through ingestion, even though that may be the mode of entry for snails which are allowed to browse, ingesting soil and/or vegetable matter. Instead, the compound appeared to enter by absorption along the exposed surfaces of the head-foot and the tissue surrounding the mantle cavity and at the pseudobranch. Following rapid accumulation of ^{14}C-label in the snail's head-foot region, reaching a maximum in about 8 h, head-foot clearance began, and an increase in concentration in the reproductive organs and digestive system was observed. Relatively high levels of ^{14}C-labelled organotin compound found in the reproductive system may explain the low tolerance and development rate noticed in subsequent generations exposed to bis(tributyltin) oxide (Cardarelli 1977; see Section 6.7.2.4). In conjunction with this, Allen *et al*. (1980) found a high concentration of ^{14}C-labelled compound (7.4 pmol Sn per 100 mg tissue) in the nuclear fraction of the head-foot tissue, possibly due to its combination with components of the cell membrane or with nuclear material. Relatively high levels of ^{14}C-labelled compound (5.4 pmol Sn per 100 mg tissue) were also observed in the mitochondrial fraction, but there were no visible alterations.

Filenko and Isakova (1979) investigated the accumulation of radioactively labelled triphenyltin chloride in *Daphnia magna* exposed to 0.01, 0.05 and 0.1 mg.L^{-1} (27, 135 and 270 nmol.L^{-1} Sn) for different time periods. The *Daphnia* were capable of concentrating the toxicant by means of absorption *through* the surface of their bodies; the authors speculated that the accumulation of the triaryltin compound could be responsible for the death of the *Daphnia*.

5.5.1.3 Metabolism

It is important to study the metabolic degradation of each organotin compound, because the biological activities of all its intermediates through to relatively nontoxic inorganic tin together determine the total biological effect (Glockling 1980). The organism's ability to weaken the injurious effect of the organotin compounds is determined in part by these metabolic processes (Stroganov et al. 1974).

Ward et al. (1981) analyzed a muscle sample from sheepshead minnows exposed to bis(tributyltin) oxide for 58 d using acid/solvent extractions and atomic absorption with a graphite furnace. The authors found 80% of the tin associated with the tributyltin fraction, 10% with the dibutyltin fraction, and the remaining 10% with monobutyltin or inorganic tin. Fish exposed to the compound for 167 d also metabolized it into the lower and less toxic alkyl moieties, as well as inorganic tin (Table 5-9). Analysis of the fish tissues at the end of the exposure period showed that the liver and viscera contained only 14 and 27% of the tributyltin moiety, respectively, as compared with 57 and 50%, respectively, for muscle and remains.

Leeuwangh et al. (1976) exposed goldfish (Carassius auratus) to triphenyltin chloride, recovering 70% as triphenyltin species, and the remainder as inorganic tin and minor amounts of diphenyltin and monophenyltin species. The authors questioned whether the triphenyltin compound was dearylated by the goldfish or by microorganisms prior to uptake.

van der Maas et al. (1972) analyzed tissues of the common pond snail (Lymnaea stagnalis) which had been exposed to 0.002, 0.01 and 0.05 $mg.L^{-1}$ triphenyltin hydroxide (5.7, 28 and 142 $nmol.L^{-1}$ Sn) for varying periods of time for tin residues by neutron-activation analysis. Because no measurable amounts of diphenyltin, monophenyltin or inorganic tin species were found, the authors concluded that most if not all of the tin was present as the unchanged triphenyltin species.

Most of these observations agree with findings on mammalian metabolism of triorganotin compounds. The in vivo sequential dealkylation or dearylation of these compounds in mammals appears to involve carbon-hydroxylated intermediates (Kimmel et al. 1977).

5.5.1.4 Clearance

The elimination or clearance of organotin residues from aquatic organisms is important, since it helps to determine the final level of compound in the organism. Ward et al. (1981), who maintained sheepshead minnows (Cyprinodon variegatus) in seawater for 28 d following a 58-d exposure to ^{14}C-labelled bis(tributyltin) oxide, observed a rapid depuration of the ^{14}C-label from all tissues. After 7 d in water free of the compound, depuration of 52% of ^{14}C in muscle, 61% in head, and 36% in viscera had occurred; by the end of the 28-d depuration period, 74% of ^{14}C residues in muscle, 64% in viscera, and 80% in head had been depurated.

Other workers have also concluded that fish are able to eliminate organotin residues. Stroganov et al. (1973), in examining the

Table 5-9. Measured tin concentrations associated with the three butyltin species and bioconcentration factors in sheepshead minnow (*Cyprinodon variegatus*) tissue exposed to bis(tributyltin) oxide for 167 d (adapted from Ward *et al.* 1981)[α].

		Tin concentration ($\mu g.kg^{-1}$) in butyltin species					
Tissue sample	Tin concentration in water ($\mu g.L^{-1}$)	Tributyl	Dibutyl	Monobutyl and inorganic	Total	Total bis(tributyltin) oxide ($\mu g.kg^{-1}$)[α]	Bioconcentration factor
Muscle	control	16	3	35	54	-	-
	solvent control	13	4	21	38	-	-
	0.18	34	15	19	68	170	x940
	0.32	50	17	28	95	238	x740
	0.48	179	58	78	315	788	x1 600
	1.0	284	136	63	483	1 210	x1 200
Viscera	control	51	60	36	147	-	-
	0.18	64	128	91	283	708	x3 900
	0.32	93	102	75	270	675	x2 100
	0.48	135	228	194	557	1 390	x2 900
	1.0	719[β]		274	993	2 480	x2 500
Liver	0.18	290	1450	920	2660	6 650	x37 000
	0.32	350	1190	1030	2570	6 420	x20 000
	0.48	1530	4800	3660	9990	25 000	x52 000
Remains	control	16	24	39	79	-	-
	1.0	150	60	90	300	750	x750
F_1 generation - whole fish	control	22	80	29	131	-	-
	0.12	43	31	52	126	315	x1 800
	0.13	65	80	60	205	512	x1 600
	0.23	317	158	99	574	1 440	x3 000
	0.44	500	320	220	1040	2 600	x2 600

Note: 1 mol Sn weighs approximately 118.7 g.

[α] Calculated based on the measured concentrations of total tin.

[β] Total tin concentration in the tri-dibutyl phase combined.

distribution of radioactive label from triethyltin chloride in the organs and tissues of carp (Cyprinus carpio), noted that the relative concentration of radioactive substance in the body of the fish increased as the radioactivity of the external medium decreased, although the absolute magnitude of uptake decreased. The authors hypothesized that this was related to the overlapping processes of accumulation and elimination of the triethyltin moiety from the organs of the carp. The higher the triethyltin chloride concentration, the more rapidly the organ or tissue was saturated with radioactive label, and the more active the elimination of the substance.

The elimination of trimethyltin residues from carp (Cyprinus carpio) exposed to 0.01 and 0.1 $mg.L^{-1}$ labelled trimethyltin chloride (0.05 and 0.5 $\mu mol.L^{-1}$ Sn) for up to 45 d was observed to occur most intensively between 7 and 15 d, with a subsequent decrease in rate (Parina et al. 1979). Leeuwangh et al. (1976) determined the rate of elimination of triphenyltin residues from the goldfish (Carassius auratus), showing that 20% was excreted with a half-time of 6 d while the remainder had a calculated half-life of 1.3 years. At this rate, the authors postulated, a lethal residue level of triphenyltin compound would be built up after a few years, even at low external concentrations of the compound.

In oysters, it has been observed that the high tin concentrations (0.93 $mmol.kg^{-1}$ dried tissue) accumulated by Crassostrea gigas exposed to organotin compounds from antifouling paints tended to be eliminated (i.e. to >0.51 $mmol.kg^{-1}$) once the concentrations of organotin compounds in the environment decreased (Alzieu et al. 1982). The ability of oysters to eliminate accumulated tin was supported by the fact that tin levels in oysters in certain areas varied little with age of specimen or with distance from polluted marinas. Waldock et al. (1983) found that the oysters C. gigas and Ostrea edulis eliminated approximately half the body burden of tributyltin species after 10 d of depuration following a 21-d exposure to 0.15 and 1.25 $\mu g.L^{-1}$ bis(tributyltin) oxide (0.51 and 4.2 $nmol.L^{-1}$ Sn), with little further loss during the next 14 d.

5.5.2 PLANTS

There is very little information on organotin burdens in plant materials and virtually nothing on uptake of organotin compounds by plants. Most studies of plant and tissue burdens have dealt with total tin which may be present as any of several organic species or as inorganic species.

Unspecified dried plant material from a Bavarian river above and below a factory producing tin compounds was analyzed for total tin. Samples from upstream contained 13-14 $mg.kg^{-1}$ Sn (0.11-0.12 $mmol.kg^{-1}$) on a dry-weight basis, while samples downstream from the factory contained 2370-3100 mg.kg^{-1} Sn (20-26 mmol.kg^{-1}), an apparent concentration factor of 170-240 (Schramel et al. 1973).

Two species of water plants, Potamogetan lucens and P. peroliatus from Lake Léman, Geneva, Switzerland, contained 4.3-12.8 mg.kg^{-1} Sn (36-108 μmol.kg^{-1}) on a dry-weight basis (Dogan and Haerdi 1980).

There have been many more studies of tin concentrations in nonaquatic plants than in aquatic plants. Measurements of tin concentrations in such plant material as alfalfa, kale, wheat flour, barley seed, and rice seed ranged from 0.09 to 13.3 mg.kg^{-1} (0.76-110 μmol.kg^{-1}) on a dry-weight basis (Schroeder et al. 1964; Bowen 1972; Byrne 1974; Omar and Bowen 1982). Plant material from sites near SnO_2 mines, dried slime ponds, tailings dunes, smelter flues, slag heaps and tin-enriched waters and muds contained higher tin concentrations, ranging from 1.5 to 2165 mg.kg^{-1} (13-18 000 μmol.kg^{-1}) on a dry-weight basis (Peterson et al. 1976, 1979).

Organotin residues on various fruit tissues sprayed with the miticides tricyclohexyltin hydroxide or hexakis (2-methyl-2-phenylpropyl) distannoxane, or on leaves sprayed with the fungicide triphenyltin hydroxide or with tricyclohexyltin hydroxide, have been detected and their concentrations measured (Getzendaner and Corbin 1972; Gauer et al. 1974; Sano et al. 1979; Hansen et al. 1981).

Samples of eight types of wood impregnated with bis(tributyltin) oxide contained 240-1350 mg.kg^{-1} bis(tributyltin) oxide (0.81-4.5 mmol.kg^{-1} Sn) on a dry-weight basis (Williams 1973). Posts impregnated with bis(tributyltin) oxide and then placed in a soil microcosm retained 93.6% of the compound 2.5 months later. Of the 6.7% released to the soil, 0.1% was found in unspecified plant materials, 0.2% was released to the air, 1.5% was found in animals and 4.5% was in the soil (Gile et al. 1982).

5.5.3 ALGAE

Hodge et al. (1979) and Seidel et al. (1980) examined representatives of nine macroalgal species from 11 sites in San Diego Bay, California, U.S.A., for total Sn(IV), and for extractable $(CH_3)_4Sn$ and extractable $(CH_3)_2SnCl_2$. Total Sn ranged from 15 to 1278 μg.kg^{-1} (0.13-11 μmol.kg^{-1} Sn) on a dry-weight basis, $(CH_3)_4Sn$ was detected in 13 of 29 samples and ranged from 0.6 to 12.5 μg.kg^{-1} (3.4-70 nmol.kg^{-1} Sn), and $(CH_3)_2SnCl_2$ was detected in 2 of 29 samples and ranged from 0.5 to 2.2 μg.kg^{-1} (2.3-10 nmol.kg^{-1} Sn). Six sites in San Francisco Bay, California, yielded macroalgae that contained 16 to 117 μg.kg^{-1} (0.13-0.98 μmol.kg^{-1} Sn) total Sn; one of eight algal samples contained a detectable level of $(CH_3)_4Sn$, 12.4 μg.kg^{-1} (69 nmol.kg^{-1} Sn). In these two groups of samples, extractable tin was less than 50% of the total tin. A concentration factor of 1.9×10^3 was calculated for algae from one site in San Diego Bay.

Ishii (1982) examined the marine algae *Ulva* sp., *Enteromorpha* sp., and *Sargasum* sp. from Mission Bay and San Diego Bay, California, for $SnCl_4$, CH_3SnCl_3, $(CH_3)_2SnCl_2$, $(CH_3)_3SnCl$, $(CH_3)_4Sn$, and butyltin. Fresh algal material was homogenized and centrifuged to obtain a particulate fraction and a supernatant fraction. The supernatant fractions contained $SnCl_4$ with decreasing amounts, respectively, of CH_3SnCl_3, $(CH_3)_2SnCl_2$, and $(CH_3)_3SnCl$. $(CH_3)_4Sn$ was not detected. The butyltin species was determined semiquantitatively and was detected in most samples. In general, samples from San Diego Bay contained more of each tin compound than samples from Mission Bay. When cultures of *Ulva* sp. were exposed to individual species of inorganic or organic tin for 5 d, the concentration factors observed were: $SnCl_4$, 130-280; CH_3SnCl_3, 40-90; $(CH_3)_2SnCl_2$, 1.6-5.9; $(CH_3)_3SnCl$, 0.8-1.4; $(CH_3)_4Sn$, <0.5. Biomethylation of $SnCl_4$ was not detected over 14 d. Evidence suggestive of biotransformation of methyltin species was obtained, but results were difficult to interpret because of contamination of organotin substrates with other organotin compounds.

Maguire *et al*. (1984) reported that *Ankistrodesmus falcatus* had an apparent bioconcentration factor of 3×10^4 for tributyltin species. About 50% of the tributyltin moiety was converted to dibutyltin species and small quantities of monobutyltin species and inorganic tin over a 4-week period at 20°C.

Callow *et al*. (1979) studied the uptake of ^{113}Sn from triphenyltin chloride in sterile seawater by *Enteromorpha intestinalis* and *Ulothrus flacca*. Uptake of tin by *E. intestinalis* spores was greater in the light than in the dark, but in *U. flacca* the converse occurred. Treatment of *U. flacca* spores with carbonyl cyanide m-chlorophenylhydrazone before addition of triphenyltin chloride caused an increase in tin uptake. This was interpreted as indicative of a light-mediated active detoxification mechanism rather than as an active exclusion mechanism.

Black and Mitchell (1952) reported that marine algae contained 0.03-3.8 $mg.kg^{-1}$ (0.25-32 $\mu mol.kg^{-1}$ Sn) on a dry-weight basis. Smith (1970) obtained values of 1.5 and 3.5 $mg.kg^{-1}$ (13 and 29 $\mu mol.kg^{-1}$ Sn) (dry weight), respectively, for *Cystoseira mediterranea* and *Fucus serratus* taken from the Gulf of Naples. This represented a concentration factor of about 10^5.

Four species of fixed algae from coastal waters in southern England contained 0.10-0.65 $mg.kg^{-1}$ (0.84-5.5 $\mu mol.kg^{-1}$ Sn) on a dry-weight basis. This represented a concentration factor of about 10^4. Phytoplankton contained about 3.5 $mg.kg^{-1}$ (29 $\mu mol.kg^{-1}$ Sn) (Smith and Burton 1972).

Blades of *Pelagophycus porra*, *Macrocystis pyrifera*, and *Eisenia arborea* from the Pacific Ocean near San Diego, California, contained 0.71-1.06 $mg.kg^{-1}$ (6.0-8.9 $\mu mol.kg^{-1}$ Sn) on a dry-weight basis. *Pelagophycus porra* pneumatocysts yielded 0.03 $mg.kg^{-1}$ (0.25

µmol.kg^{-1} Sn) in inner tissue and 0.34 mg.kg^{-1} (2.9 µmol.kg^{-1} Sn) in pigmented tissue (Hodge et al. 1979).

Mixed plankton (mainly Ceratium and Cladocera) from Lake Léman, Geneva, Switzerland, contained 5.0 mg.kg^{-1} total tin (42 µmol.kg^{-1}) (Dogan and Haerdi 1980). Sargassum lacerifolium, Ecklonia radiata, and Cystophora moniliformis from St. Vincent's Gulf, Australia, contained 0.53, 1.11 and 0.34 mg.kg^{-1} total tin (4.5, 9.3, 2.9 µmol.kg^{-1}), respectively.

5.5.4 FUNGI

Because of the widespread use of organotin compounds as antifungal agents, it is surprising that there is no published information on cellular burdens, intracellular location, or mode of uptake of tin in fungi. One report describes the degradation of bis(tributyltin) oxide to di- and monobutyltin compounds by culture filtrates from each of three fungi isolated from wood joinery (Orsler and Holland 1982). A third metabolite suspected of being a hydroxylated dibutyltin compound was also detected.

5.5.5 BACTERIA

^{14}C-labelled bis(tributyltin) oxide was gradually degraded to $^{14}CO_2$ in fertile soils, but not in sterilized soil samples, confirming microbial participation in degradation of organotin compounds (Barug and Vonk 1980). Microorganisms also participate in the degradation of organotin compounds in aquatic systems.

Yamada et al. (1978) showed that tripropyltin chloride was taken up over a period of 15 min by Escherichia coli. Uptake was independent of temperature over the range 0 to 100°C, and uptake was inhibited when cells were treated with surface-active agents prior to exposing them to tripropyltin chloride. Divalent cations inhibited uptake but monovalent cations had no effect. Tripropyltin chloride was adsorbed by protoplast membranes, by cell envelopes isolated from the bacterium, and by artificial vesicles prepared from cholesterol and phospholipids. These observations led to the conclusion that tripropyltin chloride interacts with cells by binding to phospholipids and phosphate compounds in the cell wall and cell membrane. However, the authors followed only the tin moiety of tripropyltin chloride, assuming that tin binding represented tripropyltin chloride binding.

Pure cultures of eight tributyltin-resistant bacteria isolated from Baltimore Harbor, Chesapeake Bay, U.S.A., accumulated the tributyltin moiety to 3.7-7.7 mg Sn (31-65 µmol Sn) per gram dry weight of cells, which represented a 350- to 850-fold concentration of the organotin compound. Starved cells accumulated as much of the tributyltin cation as did cells provided with glucose, suggesting that uptake was not an active transport phenomenon. Cells exposed to the tributyltin compound for 2 h were then disrupted. The unaltered tributyltin moiety was associated with fragments of the cell envelope and was removed from intact cells by EDTA. These observations led to the conclusion that the tributyltin moiety is bound to the cell surface, but is not metabolized (Blair *et al.* 1982). Jonas and Cooney (1983) isolated six microorganisms from Chesapeake Bay which were resistant to dimethyltin species. Each isolate was exposed to dimethyltin and tributyltin species, and to stannic chloride. Starved cells accumulated tin from the tributyltin compound and stannic chloride rapidly, concentrating tin up to 220 times; tin made up as much as 2% of the cell dry weight. Conversely, tin from the dimethyltin compound made up less than 0.07% of cell dry weight whether cells were starved or incubated in the presence of glucose. Thus, resistance to dimethyltin species may be by exclusion of the compound. Evidence from one of the isolates, a *Pseudomonas*, suggested that accumulation of tin from tributyltin compounds and stannic chloride was not an active cellular process because tin concentrations were identical in killed cells and in starved, viable cells. In the presence of glucose, cells accumulated only half as much stannic chloride but 1.5 times as much tributyltin compound as did starved cells.

6.0 EFFECTS ON AQUATIC ORGANISMS

6.1 INTRODUCTION

There is an abundance of literature concerning the physiological and biochemical effects of organotin compounds on mammals (see, for example, Aldridge and Street 1970, 1971; Rose 1971; Luijten 1972; Piver 1973; Luijten and Klimmer 1975; McCollister and Schober 1975; NIOSH 1976; Selwyn 1976; Aldridge 1976, 1978; Cain and Griffiths 1977; Aldridge *et al*. 1977, 1981; Smith 1978; WHO 1980; Duncan 1980; Dyer *et al*. 1982; Hayes 1982). In general, mono- and disubstituted organotin compounds are less toxic than triorganotin compounds. Tetrasubstituted organotin compounds tend to be metabolized to triorganotin compounds. The toxicity of trialkyltin compounds tends to decrease as the number of carbon atoms in the alkyl chain increases.

In comparison with the amount of research performed on the effects of organotin compounds on mammalian systems, there is relatively little information available on the effects of these toxicants on aquatic organisms, especially nontarget organisms. This information could be used to find a range of concentrations of organotin compounds that destroy specific target organisms with minimal effects on other aquatic organisms. In this chapter, the information that is available on effects of organotin compounds on both target and nontarget aquatic organisms will be reviewed and discussed in terms of biochemical, physiological, behavioral and reproductive processes.

6.2 MAMMALS, BIRDS, REPTILES

At the present time, there does not appear to be any information available relating to the effects of organotin compounds on aquatic mammals, birds or reptiles. Several reviews have examined the effects of organotin compounds on mammals, in general (see, for example, NIOSH 1976; WHO 1980; Duncan 1980).

6.3 AMPHIBIANS

One of the first observations of the effects of organotin compounds on animals was made by Jolyet and Cahours (1869), who placed crystals of triethyltin sulfate under the skin of the foot of a frog. The frog initially became agitated, then exhibited a general weakening of voluntary movements followed by respiratory distress.

One group of workers (Laughlin and Lindén 1982) has examined the effects of low concentrations of triorganotin compounds on the survival and growth of developing embryos of the freshwater frog, *Rana temporaria*. During a 5-d exposure to 0.3, 3 and 30 $\mu g.L^{-1}$ bis(tributyltin) oxide and tributyltin fluoride (~1, 10, 100 $nmol.L^{-1}$ Sn), all larvae hatched during the last 2 d of the experiment. At 0, 0.3 and 3 $\mu g.L^{-1}$ tributyltin compound (0, 1, 10 $nmol.L^{-1}$ Sn), at least 80% of the tadpoles survived; at 30 $\mu g.L^{-1}$ (100 nmol.L Sn), mortality was 40 and 50% for bis(tributyltin) oxide and tributyltin fluoride, respectively.

Only at 30 $\mu g.L^{-1}$ bis(tributyltin) oxide and tributyltin fluoride (100 $nmol.L^{-1}$ Sn) was there a noticeable decrease in wet weights of exposed tadpoles, with those exposed to tributyltin fluoride exhibiting a slightly lower mean size than the bis(tributyltin) oxide group. Tadpoles exposed to both tributyltin compounds always exhibited higher mean dry weights than the controls, although the increases were not consistently dose-dependent, possibly because of the protective nature of the jelly coating around the egg which could allow only limited amounts of tributyltin compounds into the developing egg. A consistent decline in percentage body water ((wet-dry)/wet weight), from ≈87% for controls to ≈74% for 30 $\mu g.L^{-1}$ tributyltin fluoride (100 $nmol.L^{-1}$ Sn) was observed. This seems to indicate that yolk utilization is being affected; normally, one would expect water content to increase with degree of development as the lipid which constitutes a major portion of the yolk is incorporated into the developing organism. Laughlin and Lindén (1982) concluded that the sensitivity of frog tadpoles resembles that of fish, and speculated that the mode of action could involve the trialkyltin compounds acting as ionophores for negatively charged ions in membranes responsible for ionic regulation.

Lethal concentrations of triorganotin compounds for frog and toad tadpoles have been determined using higher concentrations of the toxicants. Floch *et al.* (1964) calculated LC_{100} values for tadpoles of the common European frog, *Rana temporaria*, exposed to bis(tributyltin) oxide and tributyltin acetate to be 0.075 $mg.L^{-1}$ (24 h) and 0.05 $mg.L^{-1}$ (48 h) for bis(tributyltin) oxide (0.25 and 0.17 $\mu mol.L^{-1}$ Sn) and 0.075 $mg.L^{-1}$ (48 h) for tributyltin acetate (0.22 $\mu mol.L^{-1}$ Sn). For triphenyltin chloride and acetate, Deschiens and Floch (1962) found a 24-h LC_{100} value of 0.25 $mg.L^{-1}$ (0.68 and 0.61 $\mu mol.L^{-1}$ Sn for the chloride and acetate, respectively) for frog and toad tadpoles; the 48-h LC_{100} value was 0.05 $mg.L^{-1}$ (0.14 and 0.12 $\mu mol.L^{-1}$ Sn for the chloride and acetate, respectively).

6.4 FISH

6.4.1 MORTALITY

Most studies of the effects of organotin compounds on aquatic organisms utilize relatively high concentrations of the toxicants in order to determine the median lethal concentration required to kill 50% of the organisms (LC_{50}). It should be pointed out, however, that what is really important is knowledge of the dose that does not kill the fish, even if the exposure is over a long period of time.

Several factors are important in determining the lethality of a particular organotin compound towards a fish, including (i) R group (Blunden and Chapman 1982; Wong et al. 1982); (ii) concentration of organotin compound (Stroganov et al. 1974; Leeuwangh et al. 1976; Buzinova 1977); (iii) duration of exposure (Leeuwangh et al. 1976; Buzinova 1977); (iv) age (stage of development) (Danil'chenko 1977); (v) route of penetration (Buzinova 1977); and (vi) physicochemical and biological processes in sediment and surface water in the vicinity of the organism (Sheldon 1975; Leeuwangh et al. 1976; Good et al. 1980). These factors are also important in determining the toxicity of organotin compounds towards aquatic organisms other than fish (see, for example, Section 6.7.2.1).

The concentration-toxicity relationship for triphenyltin chloride and three freshwater fish species was examined by Leeuwangh et al. (1976). Because the relationship was linear over the range of doses tested (instead of becoming asymptotic to the time axis), no extrapolations could be made to the concentrations of triphenyltin chloride which would cause insignificant mortality of the fish over long periods of exposure.

The toxicity of triphenyltin chloride was compared with those of its degradation products - diphenyltin dichloride, monophenyltin trichloride and inorganic tin - by Leeuwangh et al. (1976). The effects of the degradation products were negligible: with $SnCl_4$, no fish died; with monophenyltin chloride, fish were killed only at the highest concentration; and with diphenyltin dichloride, concentrations several times higher than those of triphenyltin chloride were required to cause the same effect. Plum (1981), using Leuciscus idus melanotus (golden orfe), also observed that bis(tributyltin) oxide was more toxic than its degradation products, and calculated that the 48-h LC_{50} values for bis(tributyltin) oxide, dibutyltin dichloride, and monobutyltin trichloride were 0.05, 1.0, and 45 $mg.L^{-1}$ (0.17, 3.3, 280 $\mu mol.L^{-1}$ Sn), respectively.

Table 6-1 is a compilation, taken from the literature, of lethal concentrations of trialkyl- and triaryltin compounds for fish. Values are arranged according to R groups, as studies have shown that the anionic radical X has little influence (Good et al. 1980; Blunden and Chapman 1982). It can be seen from the table that different LC_{50} values have been calculated for the identical combination of trialkyl- or triaryltin compound and species of fish. It is therefore apparent that such experimental conditions as temperature, pH, water hardness and size of fish must to some extent affect the toxicity of the organotin compound. Any proposed "safe threshold" for aquatic organisms should take all these factors into consideration.

6.4.2 GROSS BEHAVIORAL AND PATHOLOGICAL CHANGES

Several investigators have studied the behavior of fish exposed to different concentrations, both lethal and sublethal, of

Table 6-1. Lethal concentrations of triorganotin compounds for fish[a].

Organotin compound	Species	Lethal concentration			Comments	Reference
		Parameter	$mg.L^{-1}$	$\mu mol.L^{-1}$ Sn		
Triphenyltin acetate	*Carassius auratus* (goldfish) (fw)	24-h LC_{100}	0.4	1.0		Gras and Rioux (1965)
		24-h LC_{100}	0.075	0.18	resistant to 0.3 $mg.L^{-1}$	Floch *et al.* (1964)
	Cyprinus carpio (carp) (fw)	24-h LC_{50}	0.521	1.3	6.9 cm long, 8.5 g	Ueda *et al.* (1961) (cited by Bock 1981)
		48-h LC_{50}	0.32	0.78		
		24-h LC_{50}	1.2	2.9	9-12 cm, 22°C	Knauf (1974) (cited by Bock 1981)
		48-h LC_{50}	0.84	2.1		
	Lebistes reticulatus (guppy) (fw)	24-h LC_{50}	0.12	0.29	1-1.5 cm, 25°C	Knauf (1974) (cited by Bock 1981)
		48-h LC_{50}	0.054	0.13		
		24-h LC_{100}	0.075	0.18	resistant to 0.02 $mg.L^{-1}$	Floch *et al.* (1964)
		48-h LC_{100}	0.03	0.07		
		7-d LC_{50}	0.032	0.08		Polster and Halacka (1971)
	Gambusia affinis (mosquitofish) (fw)	24-h LC_{100}	0.4	1.0		Gras and Rioux (1965)
	Anguilla anguilla (eel) (fw)	24-h LC_{100}	0.4	1.0		Gras and Rioux (1965)
	sunfish (species unknown) (fw)	48-h LC_{100}	1	2.5	in pond	Seiffer and Schoof (1967)
	Idus idus melanotus	24-h LC_{50}	0.18	0.44	5-7 cm, 22°C	Knauf (1974) (cited by Bock 1981)
		48-h LC_{50}	0.11	0.27		
Lirostanol (20% triphenyltin acetate)	*Rasbora heteromorpha* (harlequin fish) (fw)	24-h LC_{50}	0.42	0.21	soft water; 20°C; estimated threshold 0.12 $mg.L^{-1}$	Alabaster (1969)
		48-h LC_{50}	0.22	0.11		
Triphenyltin chloride	*Carassius auratus* (goldfish) (fw)	24-h LC_{100}	0.25	0.68		Floch and Deschiens (1962)
		48-h LC_{100}	0.25	0.68		
	Stickleback (spawn) (species unknown) (fw)	24-h LC_{100}	0.25	0.68		Floch and Deschiens (1962)
		48-h LC_{100}	0.25	0.68		
Triphenyltin fluoride	*Alburnus alburnus* (bleak) (sw)	96-h $LC(I)_{50}$[b]	0.34-0.46	0.96-1.3	10°C	Lindén *et al.* (1979)
Triphenyltin hydroxide	*Lepomis macrochirus* (bluegill) (fw)	48-h TL_m	0.033	0.094		FAO (1969) (cited by Jensen 1977)
	Rasbora heteromorpha (harlequin fish) (fw)	24-h LC_{50}	0.062	0.18	soft water, 20°C	Tooby *et al.* (1975)
		48-h LC_{50}	0.042	0.12		
	Salmo gairdneri fry (rainbow trout) (fw)	24-h LC_{50}	0.078	0.22	hard water, 15°C	Tooby *et al.* (1975)
		48-h LC_{50}	0.03	0.085		
		96-h LC_{50}	0.015	0.043		
Erithane (20% triphenyltin hydroxide)	*Rasbora heteromorpha* (harlequin fish)	24-h LC_{50}	0.36	0.21		Tooby *et al.* (1975)
		48-h LC_{50}	0.23	0.13		
		96-h LC_{50}	0.07	0.04		
Tricyclohexyltin hydroxide	*Microterus salmonoides* (largemouth bass) (fw)	24-h LC_{50}	0.06	0.2		Anon. (1979) (cited by Blunden *et al.* 1984b)
Bis(tributyltin) oxide	*Lebistes reticulatus* (guppy) (fw)	24-h LC_{100}	0.075	0.25	resistant to 0.03 $mg.L^{-1}$	Floch *et al.* (1964)
		7-d LC_{50}	0.039	0.13		Polster and Halacka (1971)

Table 6-1. (Cont'd)

Organotin compound	Species	Lethal concentration			Comments	Reference
		Parameter	mg.L^{-1}	µmol.L^{-1} Sn		
Bis(tributyltin) oxide (cont'd)	*Lebistes reticulatus* (guppy) fry (fw)	24-h LC_{50}	0.01- 0.02	0.034- 0.068		Schatzberg and Harris (1978)
	Carassius auratus (goldfish) (fw)	24-h LC_{100}	0.075	0.21	resistant to 0.03 mg.L^{-1}	Floch *et al.* (1964)
	Ictalurus punctatus (channel catfish) (fw)	96-h LC_{50}	0.012	0.040		Slesinger (1979) (cited by Argaman *et al.* 1984)
	Pimephales promelas (fathead minnow) (fw)	96-h LC_{50}	0.045- 0.2	0.015- 0.067	raw wastewater	Argaman *et al.* (1984)
	Solea solea (North Sea sole) (sw)	48-h LC_{50}	88 8.5	300 29	adult larvae	Thain (1983)
		96-h LC_{50}	36 2.1	120 7.1	adult larvae	
	Agonus cataphractus (teleost) (sw)	48-h LC_{50} 96-h LC_{50}	26 16	88 54	adult adult	"
(>98% pure)	*Alburnus alburnus* (bleak) (sw)	96-h $LC(I)_{50}$	0.013- 0.017	0.044- 0.057	10°C	Lindén *et al.* (1979)
	Cyprinodon variegatus (sheepshead minnow) (sw)	7-d LC_{50} 14-d LC_{50} 21-d LC_{50}	0.018 0.0010 0.00096	0.061 0.0034 0.0032		Ward *et al.* (1981)
	Tilapia nilotica (jewel fish) (fw)	24- to 48-h LC_{70}	0.045	0.15	0.015-0.03 mg.L^{-1}, no deaths after 15 d	Deschiens *et al.* (1966)
	Tilapia mossambica (Mozambique mouth-brooder) (fw)	24-h LC_{50}	0.028	0.094	lethal threshold between 0.008 and 0.016 mg.L^{-1}	Matthiessen (1974)
(95%)	*Salmo gairdneri* (rainbow trout) (fw)	24-h LC_{50} 48-h LC_{50}	0.028 0.021	0.094 0.071	hard water	Alabaster (1969)
	Leuciscus idus melanotus (golden orfe) (fw)	48-h LC_{50}	0.05	0.17		Plum (1981)
Tributyltin fluoride	*Alburnus alburnus* (bleak) (sw)	96-h $LC(I)_{50}$	0.006- 0.008	0.02- 0.03	10°C	Lindén *et al.* (1979)
Tributyltin chloride	*Lebistes reticulatus* (guppy) (fw)	7-d LC_{50}	0.021	0.065		Polster and Halacka (1971)
Tributyltin oleate	*Lebistes reticulatus* (guppy) (fw)	7-d LC_{50}	0.033	0.058		Polster and Halacka (1971)
Tributyltin benzoate	*Lebistes reticulatus* (guppy) (fw)	7-d LC_{50}	0.025	0.061		Polster and Halacka (1971)
Tributyltin laurate	*Lebistes reticulatus* (guppy) (fw)	7-d LC_{50}	0.030	0.061		Polster and Halacka (1971)
Tributyltin acetate	*Lebistes reticulatus* (guppy) (fw)	7-d LC_{50}	0.028	0.080		Polster and Halacka (1971)

[a] TL_m = mean threshold level; fw = freshwater; sw = seawater (marine).

[b] Initial concentration of substance killing 50% of test organisms.

trialkyl- and triaryltin compounds. Chliamovitch and Kuhn (1977), for example, found that freshwater *Salmo gairdneri* (rainbow trout) and *Tilapia rendalli* (an African food fish) exposed to 1170 µg.L^{-1} bis(tributyltin) oxide (3.9 µmol.L^{-1} Sn) exhibited agitated behavior, air gulping, and accelerated ventilation with arrhythmic and convulsive mouth and opercular movements, prior to death. Symptoms were less acute at 11.7 µg.L^{-1} (39 nmol.L^{-1} Sn), with fish progressively showing signs of tiredness and losing positive rheotaxis (ability of fish to orientate to direction of water flow) following a period of weakness and apathy. No increase in opercular movement was observed. At an intermediate concentration of 117 µg.L^{-1} (0.39 µmol.L^{-1} Sn), the fish lost positive rheotaxis at different rates. At all three concentrations, modifications of body pigmentation were observed: more pronounced body stripes for *T. rendalli* and darkened yellow iris for *S. gairdneri*.

Good *et al.* (1980) exposed the estuarine fish *Gambusia affinis* (mosquitofish), *Poecilia latipinna* (sailfin molly) and *Fundulus grandis* (gulf killifish) to tributyltin acetate at concentrations ranging from 0.2 to 1.0 mg.L^{-1} (0.57-2.9 µmol.L^{-1} Sn). Distress symptoms preceding the death of these fish included (i) erratic swimming movements; (ii) loss of equilibrium and orientation; (iii) convulsions; and (iv) loss of buoyancy.

Several Russian researchers have made similar observations in experiments using freshwater carp (*Cyprinus carpio*). Stroganov *et al.* (1974), for example, found that exposure of fish to 1 mg.L^{-1} triethyltin chloride (4 µmol.L^{-1} Sn) for 3-4 d led to a sharp decrease in activity, impairment of respiratory rhythm, and disruption of equilibrium prior to death after 7 or 8 d. No major behavioral changes were observed for fish exposed to 0.1 and 0.01 mg.L^{-1} triethyltin chloride (0.4 and 0.04 µmol.L^{-1} Sn), except for a slight loss of activity after a 40-d exposure to the higher concentration. Similarly, Buzinova (1977) observed that carp exposed to 0.5 mg.L^{-1} triethyltin chloride (2 µmol.L^{-1} Sn) exhibited disturbances in coordination of movements, respiratory rhythm, etc. after 2 d, 1-3 d prior to death. Putintsev and Gameza (1980), on the other hand, observed lethargy and loss of appetite in carp after a 20-d exposure to 0.05 mg.L^{-1} trimethyltin chloride (0.25 µmol.L^{-1} Sn), 1 week before death.

The observations of Leeuwangh *et al.* (1976), who exposed three freshwater fishes, *Rutilus rutilus* (roach), *Carassius auratus* (goldfish) and *Lebistes reticulatus* (guppy), to concentrations of triphenyltin chloride between ≈10 and 120 µg.L^{-1} (27 and 325 nmol.L^{-1} Sn), agree with those of other investigators. Prior to death, excessive mucus production, loss of equilibrium, immobilization, opaque eyes, hemorrhaging and fin rot were noted. The higher the concentration of organotin compound, the more quickly the more pronounced symptoms were produced. Leeuwangh *et al.* (1976) also found that fish exposed to high concentrations of diphenyltin compounds exhibited loss of equilibrium, immobility and pigmentation 24 h before death.

Matthiessen (1974) found that the freshwater fish Tilapia mossambica (Mozambique mouthbrooder) exposed to bis(tributyltin) oxide at concentrations just below 8 $\mu g.L^{-1}$ (27 $nmol.L^{-1}$ Sn) became sluggish, had difficulty balancing, and stopped feeding. Sexual display patterns were not produced. Fish appeared pale because skin melanophores did not expand. Opacity of the cornea occurred across the middle of the eye. After several weeks many sublethal effects disappeared, leading Matthiessen (1974) to suggest that the fish were able to adapt to the organotin compound.

In summary, the gross behavioral and pathological symptoms prior to death which are common to most freshwater and marine fish species that have been experimentally exposed to low concentrations (≈10-1000 $\mu g.L^{-1}$) of trialkyl- and triaryltin compounds include sluggishness, loss of appetite, disruption of equilibrium and corneal lesions.

6.4.3 ORGAN AND TISSUE CHANGES

Pathological changes resulting from exposure to triorganotin compounds have been observed in four tissues and organs in fish: kidney, liver, gills and cornea. In freshwater rainbow trout (Salmo gairdneri) fry exposed to 5 $\mu g.L^{-1}$ tributyltin chloride (15 $nmol.L^{-1}$ Sn) for 10 d (at which time death occurred), extensive hydropic degeneration of the tubular epithelial cells in the kidney was observed (Seinen et al. 1981); the authors suggested that these fluid transporting epithelial cells have a great demand for ATP which would make them extremely sensitive to an energy shortage caused by the inhibition of mitochondrial energy conservation by the trialkyltin compound. No histological changes in the kidneys were noted at 0.2 and 1 $\mu g.L^{-1}$ tributyltin chloride (0.62 and 3.1 $nmol.L^{-1}$ Sn).

In Salmo gairdneri fry exposed to 0, 0.2 and 1 $\mu g.L^{-1}$ tributyltin chloride (0, 0.62 and 3.1 $nmol.L^{-1}$ Sn) for 110 d, a dose-related increase in relative liver weights was observed along with histopathological alterations, including hyperplasia of liver cells (Seinen et al. 1981). At 1 $\mu g.L^{-1}$ tributyltin chloride (3.1 $nmol.L^{-1}$ Sn), the nuclei of the hepatocytes were arranged in rosettes and the cytoplasm was swollen and vacuolated. There was a dose-related increase in the total area of the liver nuclei because of an increase in the number of liver cells, whereas the area of glycogen storage decreased as the dose increased (see Section 6.4.4). Chliamovitch and Kuhn (1977) also found microscopic changes in the livers of S. gairdneri exposed to low concentrations of bis(tributyltin) oxide (11.7 $\mu g.L^{-1}$ (39 $nmol.L^{-1}$ Sn)) (Section 6.4.4). These changes consisted of damage to the biliary columnar epithelial cells which were separated from the connective tissue and flattened. Hepatocytes remained unimpaired but the sinusoides (endothelium-lined passages for blood in liver tissues) were always congested.

In addition to alterations in liver and kidney tissue, the gill epithelium appears to be affected by low concentrations of trialkyltin compounds. Chliamovitch and Kuhn (1977) observed a separation of the gill epithelium from the basement membrane and pillar cells, and swelling of the secondary lamellae and dilation of the vessels were observed in rainbow trout exposed to 5.85 $mg.L^{-1}$ bis(tributyltin) oxide (20 $\mu mol.L^{-1}$ Sn) for 10 min. Marked swelling of mitochondria, tubular reticulum and perinuclear space of chloride cells was also noted, accompanied by complete disorganization of cristae and rupture of the mitochondrial membranes. Mitochondrial swelling is apparently a consistent effect of trialkyltin poisoning (Selwyn et al. 1970; Aldridge 1978). A 20-min exposure to 1.17 $mg.L^{-1}$ bis(tributyltin) oxide (3.9 $\mu mol.L^{-1}$ Sn) caused the lumen of the tubular reticulum to accumulate a dark substance, indicating ion transport modifications (Chliamovitch and Kuhn 1977); vasodilation and much blood in the gill vessels were also observed. In addition, increased mucus secretion from the skin epithelium was observed. The authors concluded that two poisoning mechanisms could take place: at high concentrations, causing rapid suffocation by destruction of the gill epithelium, and at low concentrations, via inhibition of major metabolic pathways. In contrast, no alterations in the gills or skin were found by Seinen et al. (1981) on exposure of rainbow trout to tributyltin chloride.

The other main tissue observed to be damaged in Chliamovitch and Kuhn's (1977) experiments was the cornea. The external epithelial layer composed of squamous surface cells was destroyed, vacuolization was noted in a single layer of basal, columnar cells and in three layers of polyhedral cells, and infiltration of leucocytes and small hemorrhages were observed in the limbus corneae. No damage occurred to the Bowman's membrane, fibroblasts of substantia propria or squamous cells of the endothelium. A lesion of the cornea was also found to be the most noticeable effect of a 24-h exposure of 0.005 $mg.L^{-1}$ bis(tributyltin) oxide (17 $nmol.L^{-1}$ Sn) to the freshwater tropical food fish Sarotherodon mossambicus (Tilapia mossambica) (Mozambique mouthbrooder) (Matthiessen 1974), and opaque eyes were observed by Leeuwangh et al. (1976) who exposed three freshwater fish species to low concentrations of triphenyltin chloride (<120 $\mu g.L^{-1}$; <325 $nmol.L^{-1}$ Sn).

6.4.4 BIOCHEMICAL AND HEMATOLOGICAL EFFECTS

Desaiah et al. (1973) observed that tricyclohexyltin hydroxide was an outstanding inhibitor of oligomycin-sensitive mitochondrial Mg^{2+}-ATPase from freshwater bluegill fish (Lepomis macrochirus) brain homogenates, with an I_{50} value (50% inhibition of enzyme) of 66 $pmol.L^{-1}$. At a higher concentration (0.2 $\mu mol.L^{-1}$), the compound was also effective on the Na^+-K^+-ATPase, with I_{50} and I_{90} values of 0.2 and 1.9 $\mu mol.L^{-1}$, respectively. This study agrees with the findings of several other investigators using in vitro preparations of mammalian mitochondrial membranes (see, for example, Aldridge and Street 1970, 1971; Aldridge 1976, 1978; Aldridge *et al*. 1977, 1981).

The Mg^{2+}- and Na^+-K^+-ATPases are not the only enzymes influenced by triorganotin compounds. Buzinova (1977) found that the activities of the digestive enzymes (amylase, trypsin, lipase) of freshwater *Cyprinus carpio* (carp) yearlings were affected by triethyltin chloride. At 0.1 and 0.5 $mg.L^{-1}$ triethyltin chloride (0.4 and 2 $\mu mol.L^{-1}$ Sn), the activities of the three enzymes decreased up to 90%; the time required for the decrease was longer for the lower concentration of toxicant. Because there were no visible signs of pathology, the author postulated that the effects on fish were determined by the rate of change of enzymatic activity; at the lower triethyltin chloride concentration, the digestive enzymes decreased in activity over a long time period, allowing physiological adaptation to the environment. Using 0.003 $mg.L^{-1}$ triethyltin chloride (13 $nmol.L^{-1}$ Sn), Buzinova (1977) also observed that the degree of influence of triethyltin chloride on the digestive function of carp was stronger when the organotin compound was introduced directly into the gut with food than when it acted only through the surface of the body (gills, integument).

Putintsev and Gameza (1980) studied the activities of alkaline phosphatase and alanine amino transferase, and determined the cholesterol content in blood serum in yearling and adult carp exposed for different periods of time (up to 45 d) to trimethyltin chloride at sublethal and lethal concentrations (0.01, 0.1 and 1 $mg.L^{-1}$; 0.05, 0.5 and 5 $\mu mol.L^{-1}$ Sn). The cholesterol content in adult carp exposed to all three concentrations of trimethyltin chloride decreased sharply in the first week, then stabilized after another week; the higher the concentration, the greater the initial decrease. The authors suggested these changes were connected with the peculiarities of lipid (especially cholesterol) exchange and the absence of distinct fat reserves in yearlings. The rapid decrease of cholesterol in the blood serum could be explained by the intensive use of cholesterol as a building material for cell membranes and as a precursor for such biologically active compounds as steroid hormones and bile acids. The higher the trimethyltin chloride concentration, the more intensive the use of cholesterol would be in the compensatory and adaptive actions of the carp.

In both yearling and adult carp exposed to 0.01-1 $mg.L^{-1}$ trimethyltin chloride (0.05-5 $\mu mol.L^{-1}$ Sn), the alkaline phosphatase activities increased for 2 weeks, after which they began to decrease towards control values. In yearlings exposed to 0.1 and 0.5 $mg.L^{-1}$ trimethyltin chloride (0.5 and 2.5 $\mu mol.L^{-1}$ Sn), the alanine amino transferase activities remained below normal values for the duration of the 45-d experiment. The changes observed in the activities of these two enzymes testify to early functional changes in the cells of the hepatopancreas; the functional activity of the endoreticulo-endothelial Kupfer cells increases and detoxifies the organotin compound. Again, the stabilization of most effects in the second half of the experiment indicated that fish can adapt to this toxicant (Putintsev and Gameza 1980).

Triorganotin compounds exert hematological as well as enzymatic effects. Chliamovitch and Kuhn (1977) examined the effects of exposures to different concentrations of bis(tributyltin) oxide for different time periods on various blood parameters of the freshwater fish, Salmo gairdneri. The main effect of a long-term exposure to a low concentration of toxicant (e.g. 23 µg.L^{-1} (77 nmol.L^{-1} Sn) for 42 h) appeared to be an increase of packed cell volume (PCV) accompanied by an increase in hemoglobin concentration; the opposite trend was observed for a short-term exposure to high concentrations of bis(tributyltin) oxide (e.g. 5850 µg.L^{-1} for 5 min; 20 µmol.L^{-1} Sn). At 1.17 mg.L^{-1} bis(tributyltin) oxide (3.9 µmol.L^{-1} Sn) for 30 min, the increase in PCV was due to a swelling of the erythrocytes; the authors suggested that this swelling was a consequence of lowered oxygen tension due to a coating effect of the organotin compound on the gills. At an exposure of 0.053 mg.L^{-1} (0.18 µmol.L^{-1} Sn) for 21.5 h, the erythrocytes shrank, and the PCV increase was due to an increase in the number of blood cells. Hemolysis, reported to be an effect of trialkyltin compounds (Byington et al. 1974), was not observed.

In contrast, Seinen et al. (1981) found a dose-related decrease in the hemoglobin concentration in rainbow trout (S. gairdneri) yolk sac fry exposed to 0, 0.2 and 1 µg.L^{-1} of tributyltin chloride (0, 0.6 and 3 nmol.L^{-1} Sn) for 110 d and 5 µg.L^{-1} (15 nmol.L^{-1} Sn) for 10 d. The number of blood cells was significantly decreased at the 1 µg.L^{-1} (3 nmol.L^{-1} Sn) level only. The authors suggested that these changes were a reflection of the overall diminished condition of the exposed fish.

The effects of trialkyltin compounds on the uptake of potassium phosphate and sodium bicarbonate from water by carp (Cyprinus carpio) have also been investigated. Filenko and Parina (1981, 1983) used triethyltin and tripropyltin chloride to study the incorporation of ^{32}P (in water as potassium phosphate) into the organs and tissues of the carp, and found that the more active the transfer of the organotin compounds into the tissues studied (blood, liver, brain, white and red muscles), the lower the effectiveness of the ^{32}P incorporation. Stroganov et al. (1974) studied the effect of different concentrations of triethyltin chloride on the uptake of sodium bicarbonate from water by freshwater carp, on the distribution of inorganic carbon in the fish organs and tissues, and on the metabolism of glycogen, protein and lipids. A 40-d exposure to 0.1 and 0.01 mg.L^{-1} (0.4 and 0.04 µmol.L^{-1} Sn) caused changes in the uptake and distribution of radiocarbon in the organ components that reflected changes in carbohydrate, fat and protein metabolism; metabolic processes in the brain, liver and muscles were disturbed, with carbohydrate metabolism being most affected. The brain was most readily subjected to the action of triethyltin chloride, because of its affinity for the toxicant and the large concentrations of phospholipids and glycogen in the brain. A substantial decrease in the specific activity of glycogen, lipids and protein indicated that new formation of these compounds in the brain was being inhibited; the rate of formation of glycogen, for example, was inhibited by 45 and 25% at 0.1 and 0.01 mg.L^{-1} (0.4 and 0.04 µmol.L^{-1} Sn), respectively. Changes were particularly marked in the liver at an exposure of 1 mg.L^{-1} triethyltin chloride (4 µmol.L^{-1} Sn) within the first 2 d of the experiment; glycogen synthesis was severely inhibited. At 0.1 mg.L^{-1} triethyltin chloride (0.4 µmol.L^{-1} Sn), the rate of incorporation of ^{14}C into liver glycogen decreased by 20%, whereas at 0.01 mg.L^{-1} (0.04 µmol.L^{-1} Sn) it increased; these findings indicate the two-phase nature of triethyltin chloride action, which first increases then decreases enzymatic activity. Because glycogen serves as an energy source, its increase may be an adaptation mechanism which safeguards the vital processes of the organism against the action of triethyltin chloride (Stroganov _et al_. 1974).

This finding agrees with the observations of Seinen _et al_. (1981), who found the liver almost completely depleted of glycogen in freshwater _Salmo gairdneri_ (rainbow trout) fry exposed to 5 µg.L^{-1} tributyltin chloride (15 nmol.L^{-1} Sn) for 10 d; diminished glycogen storage was also noted after a 110-d exposure to 0.2 and 1 µg.L^{-1} tributyltin chloride (0.6 and 3 nmol.L^{-1} Sn). The authors explained this diminished glycogen storage as well as a dose-related decrease in growth rate of fish exposed to tributyltin chloride (see Section 6.4.5) by the inhibitory effect of triorganotin compounds on mitochondrial energy conservation. During the transitional phase between the yolk sac fry stage and the swimming fry stage, trout fry use triglycerides mainly as fuel, and could be exposed to high amounts of the lipophilic tributyltin chloride. In addition, their activity is strongly increased, requiring high energy. Their sudden death after this transition could therefore be explained by an acute energy shortage.

6.4.5 REPRODUCTION, GROWTH AND DEVELOPMENT

It is important to study the effects of organotin compounds on reproduction, growth and development, because exposure to sublethal concentrations could lead to serious reductions in the productive capacity of natural fish populations.

In a study examining the potential of tris(4-butylcyclohexyl)-tin dodecanoate as a chemosterilant, Kenaga (1975) exposed adult sticklebacks (probably _Eucalin inconstans_) to 0.1 mg.L^{-1} of the compound in brackish water. The adults appeared normal in all respects, the males were observed to build typical nests and the females oviposited, yet no fry were observed after 3 weeks; the control group produced a large population of stickleback fry which grew normally.

Ward _et al_. (1981) exposed marine sheepshead minnows (_Cyprinodon variegatus_) for 167 d to bis(tributyltin) oxide which varied in concentration from 1.5 to 8.5 nmol.L^{-1} Sn over the exposure period.

Several aspects of reproduction and growth were not significantly affected by exposure to bis(tributyltin) oxide in this experiment: (i) growth of the parental fish; (ii) total number of eggs spawned by the parental fish; (iii) hatching success of juveniles from embryos produced by parental fish; (iv) time required for hatching; (v) juvenile mortality for 28 d after hatching as a function of duration of exposure of parental fish to bis(tributyltin) oxide (the mortality of juveniles was higher in 2.0 and 3.8 nmol.L^{-1} Sn than in the controls, but there was not a statistically significant concentration-response relationship because of variability in mortality data); and (vi) growth of surviving F$_1$ juveniles to 28 d after hatching. Ward *et al.* (1981) concluded that the chronic toxicity of bis(tributyltin) oxide was not significantly greater than its acute toxicity to sheepshead minnows, even though bioaccumulation occurred (see Section 5.5.1.2).

Rainbow trout (*Salmo gairdneri*) yolk sac fry were exposed to 0, 0.2, 1 and 5 µg.L^{-1} tributyltin chloride (0, 0.6, 3 and 15 nmol.L^{-1} Sn) for 110 d (Seinen *et al.* 1981). After transition of the yolk sac fry to swimming fry (≈10-12 d), all fry exposed to 5 µg.L^{-1} tributyltin chloride (15 nmol.L^{-1} Sn) died. There were no other mortalities. However, dose-related retardation of growth was observed at 0.2 and 1 µg.L^{-1} tributyltin chloride (0.6 and 3 nmol.L^{-1} Sn); fish exposed to 1 µg.L^{-1} (3 nmol.L^{-1} Sn) had mean body weights only 56% of those of controls at the end of the experimental period. The authors suggested that this dose-related decrease in growth rate may be explained by the inhibitory effect of triorganotin compounds on mitochondrial energy conservation.

Similarly, Matthiessen (1974) found that long-term exposure of the freshwater tropical food fish *Tilapia mossambica* (*Sarotherodon mossambicus*) (Mozambique mouthbrooder) to 8 µg.L^{-1} bis(tributyltin oxide) (27 nmol.L^{-1} Sn) for 5 weeks caused the fish to lose weight; weight gains at 5 µg.L^{-1} (17 nmol.L^{-1} Sn), however, were comparable with those of controls. The weight loss experienced during exposure to the higher concentration of trialkyltin compound could not be explained by reduced food intake; instead the author suggested it was partly caused by higher levels of activity, and thus increased energy requirements, resulting from aggressive behavior exhibited by these fish. Danil'chenko and Stroganov (1975) noted a dose-related increase in length of larvae of three freshwater bony fishes exposed to triethyltin chloride at 0.001, 0.01, 0.1 and 1.0 mg.L^{-1} (4, 40, 400 and 4000 nmol.L^{-1} Sn).

Danil'chenko (1977) investigated the embryonic development of freshwater loach (*Misgurnus fossilis*) and three species of sturgeons (*Acipenser güldenstädt*, *A. stellatus* and *A. nudiventris*) exposed to triethyltin chloride, tripropyltin chloride and dimethyltin chloride. By determining the concentrations of organotin compound at which individual stages of embryogeny could be completed, he found that, in general, the fish eggs were more resistant to the effect of organotin compounds at the time of fertilization and commencement of development than were prolarvae and larvae. In the case of loach eggs, for example, although fertilization was possible at 5 mg.L^{-1} triethyltin chloride (21 µmol.L^{-1} Sn), the prolarvae and larvae were able to survive only at concentrations 100-500 times less. Resistance declined even more strongly during the embryonic development of sturgeons. For example, although fertilization was possible at 10 mg.L^{-1} triethyltin chloride (42 µmol.L^{-1} Sn), the larvae could survive only at 0.01 mg.L^{-1} (42 nmol.L^{-1} Sn), a 10 000-fold decrease in resistance. Danil'chenko (1977) hypothesized that the greater resistance of these first stages was connected with the fact that the cytoplasm of the egg contains all the necessary components (e.g. DNA, RNA) for the morula and blastula stages. Because the internal resources of the egg are not sufficient to guarantee the success of the gastrulation and subsequent stages, the resistance of the eggs becomes less than that in the first stages.

Danil'chenko (1977) also determined the survival of loach larvae exposed to triethyltin chloride in relation to the stage of development at which exposure occurred in order to assess the sensitivity of loach eggs in the first 90 min of development (before the first cleavage division) and between the time of fertilization and the middle of gastrulation. The sensitivity of the development stage was assessed from the life span. In general, fish eggs were most sensitive to triethyltin chloride at the time of fertilization and at the time of cleavage of the fertilized egg; sensitivity declined during subsequent development. This was explained by the fact that subsequent development depends on the proper completion of processes taking place in the zygote and developing embryo.

6.5 ARTHROPODS - CRUSTACEANS

6.5.1 LOBSTERS, CRABS AND SHRIMPS

Several factors have been found to influence the toxicity of organotin compounds towards the decapods lobster, crab and shrimp:

(i) Structure of Compound

Laughlin *et al.* (1984a) exposed marine mud crab larvae (*Rhithropanopeus harrisii*) for the duration of zoeal development (10-12 d) to eight triorganotin compounds dissolved in seawater. The correlation between the toxicity (LC_{50}) of each toxicant and its total surface area (TSA) was excellent (Figure 6-1), suggesting that aqueous solvation free energy governs the uptake, and thus biological action, of triorganotin compounds towards mud crabs (see also Section 5.5.1.1). Laughlin (1984) has recommended the use of quantitative structure-activity relationships (QSAR) for estimating biological effects by using existing information to evaluate unstudied organotin compounds.

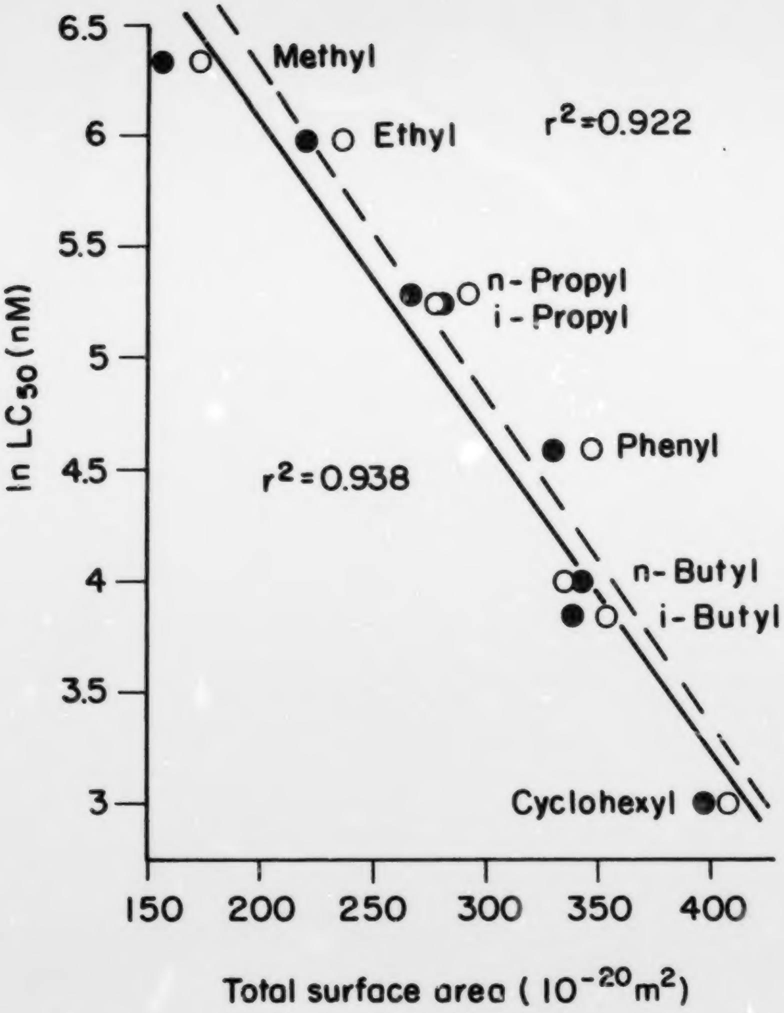


Figure 6-1. Correlation between computed molecular surface area (TSA) and natural log LC_{50} values for eight triorganotin compounds (as indicated by R group) to the mud crab, Rhithropanopeus harrisii. Prediction lines for 4-coordinate (—●—) and 5-coordinate (--o--) tin TSA estimates are compared (from Laughlin *et al*. 1984a).

Laughlin and French (1980) found that the toxicity of homologous alkyltin compounds to crab (Hemigrapsus nudus) larvae increased as the carbon number of the alkyl moiety decreased from C_4 to C_2; the trend was reversed for trimethyltin hydroxide.

(ii) *Temperature and Salinity*

Wright and Roosenburg (1982) determined the toxicity of trimethyltin chloride to stage I zoeae of the marine fiddler crab, Uca pugilator, at different temperatures and salinities. In general, it was found that an increase in temperature and a decrease in salinity together sharply increased the toxicity of the compound towards the zoeae. At constant temperatures, increasing salinity had little effect on toxicant-induced mortality, whereas at constant salinity, decreasing temperature reduced toxicant-induced mortality. The LC_{50} values for Uca pugilator zoeae exposed to trimethyltin chloride at different temperature-salinity combinations are compiled in Table 6-2. It can be seen that an increase in salinity from 20 to 30^0/oo at 28°C requires almost a 10-fold increment in trimethyltin chloride concentration to affect the 24-h LC_{50}. The sharp fall in LC_{50} values between 24 and 48 h demonstrates the importance of exposure time in determining toxicity.

(iii) Concentration of Toxicant/Duration of Exposure

Laughlin and French (1980) studied the acute toxicity of trialkyltin compounds to marine zoeal shore crabs (Hemigrapsus nudus) and lobster larvae (Homarus americanus). All concentrations of alkyltin compounds tested were acutely toxic to the crab zoeae; most larvae died by the 8th day of exposure. In general, survival time increased with decreasing concentrations. The authors did not calculate LC_{50}'s because they found that (1) toxicity was not asymptotic witn time, and (2) susceptibility to toxicants drastically increased at ecdysis (which occurred between 7 and 10 d in control larvae). Instead, they roughly estimated the times for 50% mortality from plots of percentage survival versus duration of exposure (Table 6-3).

Laughlin and French (1980) found that lobster larvae were much more sensitive to bis(tributyltin) oxide than were shore crab larvae. A 24-h exposure to 20 $\mu g.L^{-1}$ bis(tributyltin) oxide (67 $nmol.L^{-1}$ Sn) killed all the lobster larvae; 5-15 $\mu g.L^{-1}$ (17-51 $nmol.L^{-1}$ Sn) was acutely toxic within 6 d, the length of survival time increasing slightly with decreasing concentrations of the tributyltin compound. Only at 1 $\mu g.L^{-1}$ bis(tributyltin) oxide (3.4 $nmol.L^{-1}$ Sn) were some larvae able to metamorphose successfully; their development rate was not significantly affected, although a comparison of dry weights indicated that growth was significantly decreased.

Table 6-2. LC_{50} values for zoeae of Uca pugilator exposed to trimethyltin (as the chloride) at different temperature-salinity combinations (from Wright and Roosenburg 1982).

Salinity ($^{0}/oo$)	Temperature (°C)	24-h LC_{50}		48-h LC_{50}	
		$mg.L^{-1}$	$\mu mol.L^{-1}$ Sn	$mg.L^{-1}$	$\mu mol.L^{-1}$ Sn
30	10	12.0	60.6	1.4	7.1
	20	3.35	16.9	0.37	1.9
	28	0.61	3.1	0.08	0.4
20	10	2.2	11	0.20	1.0
	20	0.4	2	0.04	0.2
	28	0.07	0.4	0.03	0.2
10	10	0.31	1.6	0.05	0.3
	20	0.015	0.076	-$^{\alpha}$	-
	28	-	-	-	-

[α] Blanks indicate insufficient information for LC_{50} determination.

Table 6-3. Survival times for zoeal shore crabs (*Hemigrapsus nudus*) exposed to triorganotin compounds (from Laughlin and French 1980).

Compound	Concentration		50% survival time (d)[a]
	$\mu g.L^{-1}$	$\mu mol.L^{-1}$ Sn	
Bis(tributyltin) oxide	100	0.34	3.4
	75	0.25	4.8
	50	0.17	5.8
	25	0.084	6.2
Tripropyltin hydroxide	100	0.38	3.5
	75	0.28	3.5
	50	0.19	4.6
	25	0.095	5.1
Triethyltin hydroxide	150	0.68	2.8
	100	0.45	3.2
	75	0.34	3.5
	50	0.23	4.8
Trimethyltin hydroxide	150	0.83	3
	100	0.56	4.4
	75	0.42	5.2
	50	0.28	6.6

[a] Values for 50% survival time are estimated from plots of percentage survival vs. duration of exposure.

Larvae of the shore crab *Carcinus maenus* exhibited greatly increased sensitivity to bis(tributyltin) oxide with increased duration of exposure, with 48-h and 96-h LC$_{50}$ values of 110 and 10 μg.L^{-1} (370 and 34 nmol.L^{-1} Sn), respectively (Thain 1983).

(iv) Stage of Development

Thain (1983) observed that sand shrimp (*Crangon crangon*) larvae were more sensitive to the effects of bis(tributyltin) oxide than were adults, with 96-h LC$_{50}$ values of 1.5 and 41 μg.L^{-1} (5.1 and 140 nmol.L^{-1} Sn), respectively.

6.5.2 AMPHIPODS

Amphipods, which are of ecological significance as important components of shallow water benthic communities, are nontarget organisms which may be detrimentally affected by the presence of organotin compounds in the aquatic environment.

6.5.2.1 Toxicity

The marine amphipods *Orchestoidea californiana* and *Gammarus oceanicus* were found to be sensitive to short-term exposures to low concentrations of bis(tributyltin) oxide and tributyltin fluoride and to tributyltin leachates from panels painted with two different antifouling paint formulations (Laughlin *et al*. 1982). For *Orchestoidea californiana*, the decrease in viability between 1 and 6 μg.L^{-1} bis(tributyltin) oxide (3.4 and 20 nmol.L^{-1} Sn) was not consistently dose-dependent compared with controls. Final survival values after 9 d were 60, 73, 53, 20 and 7% (80% survival for controls) in 1, 3, 6, 10 and 15 μg.L^{-1} bis(tributyltin) oxide, respectively (3.4, 10, 20, 34 and 51 nmol.L^{-1} Sn). There was no significant toxicity difference between the two triorganotin compounds. It is important to note that the toxicity of bis(tributyltin) oxide and tributyltin fluoride became apparent only after 5 d of exposure of *Orchestoidea californiana*, suggesting that short-term toxicity tests may seriously underestimate toxicity and yield values much higher than the maximum acceptable toxicant concentration. The toxicity of the paint formulations to *Gammarus oceanicus* in these short-term tests showed a close correlation to the painted surface area and the tributyltin leaching rate.

To determine the effects of long-term exposure of the Baltic amphipod *Gammarus oceanicus* to bis(tributyltin) oxide and tributyltin fluoride, Laughlin *et al*. (1984b) exposed adults and larvae to these compounds for 8 weeks or to leachates from antifouling paints containing tributyltin fluoride for 5 weeks. At 0.3 μg.L^{-1} (1 nmol.L^{-1} Sn) there was good adult survival for at least 2 weeks, while at 3 μg.L^{-1} (10 nmol.L^{-1} Sn) 50% died after a 10- to 12-d exposure and none survived for

8 weeks. All amphipods exposed to one of the paints that leached tributyltin species at a rate 10 times higher (5.5 $\mu g.L^{-1}$ in 48 h; 18-19 $nmol.L^{-1}$ Sn) than that of the second paint (0.5 $\mu g.L^{-1}$ in 48 h; 1.6-1.7 $nmol.L^{-1}$ Sn) died in 7 d. After 8 weeks' exposure, larval survival was as follows: 127 and 184 larvae in seawater and acetone controls; 44 and 79 larvae in 0.3 $\mu g.L^{-1}$ tributyltin fluoride and bis(tributyltin) oxide (1 $nmol.L^{-1}$ Sn); and 0 larvae in 3 $\mu g.L^{-1}$ (10 $nmol.L^{-1}$ Sn) of the two compounds. No larvae survived in the fast leaching paint, while about 40 survived in the tank with the slow leaching paint.

The authors concluded from this second study that tributyltin compounds are slow-acting toxins at very low concentrations, and suggested the need for more long-term studies of the sublethal effects of trialkyltin compounds on aquatic organisms.

6.5.2.2 Growth

In terms of sublethal effects, Laughlin *et al.* (1984b) found reduced or blocked release of larvae from *Gammarus oceanicus* females exposed to 0.3 $\mu g.L^{-1}$ bis(tributyltin) oxide or tributyltin fluoride (1 $nmol.L^{-1}$ Sn) for several weeks. Growth of larvae exposed to bis(tributyltin) oxide for 8 weeks was decreased significantly, whereas that for larvae exposed to tributyltin fluoride was increased, possibly because mortality resulted in such low larval densities that growth accelerated.

6.5.2.3 Mechanism of action

Laughlin *et al.* (1984b) found no effect of long-term exposure of *Gammarus oceanicus* to 0.3 or 3 $\mu g.L^{-1}$ of tributyltin compounds (1, 10 $nmol.L^{-1}$ Sn) on oxygen consumption rates of whole organisms. Because tributyltin compounds are known to cause a variety of effects on mitochondria which include increases in oxygen consumption (Aldridge 1976), the authors speculated that the effect of low concentrations of tributyltin compounds on amphipods may be mediated only in part, if at all, by direct effects on mitochondria.

6.5.2.4 Behavior

Laughlin *et al.* (1982) exposed two species of marine amphipods, *Orchestoidea californiana* and *Gammarus oceanicus*, to 10 and 15 $\mu g.L^{-1}$ bis(tributyltin) oxide and tributyltin fluoride (~30, 45 $nmol.L^{-1}$ Sn), noting a loss of orientation and feeding behavior, with the limb or swimming movements being ataxic and very poorly coordinated. Laughlin *et al.* (1984b) observed the behavior of larval *Gammarus oceanicus* exposed for long periods of time to lethal concentrations of bis(tributyltin) oxide or tributyltin fluoride to be highly abnormal prior to death. The larvae first displayed excessive swimming behavior, then swam to the surface and stuck to the surface film. Laughlin *et al.* (1984b) also noted behavior suggesting that the amphipods are capable of sensing the compounds and possibly exhibiting an escape response which may protect natural populations from acute intoxication.

6.5.3 COPEPODS

Copepods, which constitute as much as 70% of the zooplankton and serve as an important food item of larval fish, are significant primary consumers in the marine food chain. In studies in which the calanoid copepod, *Acartia tonsa*, was exposed to low concentrations of bis(tributyltin) oxide (0.3-3.0 µg.L^{-1}; 1-10 nmol.L^{-1} Sn), the 96-h and 144-h LC$_{50}$ values were found to be 1.0 and 0.55 µg.L^{-1} (3.4 and 1.9 nmol.L^{-1} Sn) (U'ren 1983). The threshold level was found to be below 0.3 µg.L^{-1} (1 nmol.L^{-1} Sn), a concentration that might be encountered in Canadian waters. In comparison, the 96-h LC$_{50}$ for *A. tonsa* exposed to copper (also used in antifouling paints) ranged between 17 and 55 µg.L^{-1} (0.27 and 0.86 µmol.L^{-1}) (Sosnowski *et al.* 1979), which suggests that bis(tributyltin) oxide is much more toxic than copper (almost 300 times on a mole per litre basis).

Lindén *et al.* (1979) determined the toxicity of three organotin compounds against the harpacticoid *Nitocra spinipes* at 21°C in brackish water. The 96-h LC(I)$_{50}$ values, in µg.L^{-1} (nmol.L^{-1} Sn), were as follows: tributyltin fluoride - 1-2 (3-6); bis(tributyltin) oxide - 1-3 (3-10); and triphenyltin fluoride - 6-10 (20-30). The harpacticoid plays an important role as a food organism for larval fish and crustacean species.

6.5.4 *DAPHNIA* AND *ASELLUS*

Polster and Halacka (1971) determined the 48-h LC$_{50}$ values for *Daphnia magna* exposed to the following compounds: tributyltin acetate (3.5 µg.L^{-1}; 10 nmol.L^{-1} Sn); tributyltin oleate (9 µg.L^{-1}; 16 nmol.L^{-1} Sn); tributyltin benzoate (4.5 µg.L^{-1}; 11 nmol.L^{-1} Sn); tributyltin chloride (4.8 µg.L^{-1}; 15 nmol.L^{-1} Sn); tributyltin laurate (4.9 µg.L^{-1}; 10 nmol.L^{-1} Sn); bis(tributyltin) oxide (2.5 µg.L^{-1}; 8.4 nmol.L^{-1} Sn); and triphenyltin acetate (90 µg.L^{-1}; 220 nmol.L^{-1} Sn). Leeuwangh *et al.* (1976) examined the dependence of mortality of the water louse (*Asellus aquaticus*) and *Daphnia magna* on the concentration of triphenyltin chloride; an average concentration of about 40 µg.L^{-1} (0.1 µmol.L^{-1} Sn) caused a median period of survival of approximately 100 h. Floch and Deschiens (1962) found a 24-h LC$_{100}$ of 0.25 mg.L^{-1} triphenyltin chloride (0.68 µmol.L^{-1} Sn) for *Daphnia longispina*; the 48-h LC$_{100}$ was 0.05 mg.L^{-1} (0.1 µmol.L^{-1} Sn). For the same species, Floch *et al.* (1964) observed an LC$_{100}$ of 0.12 mg.L^{-1} (0.4 µmol.L^{-1} Sn) in 24 h and 0.06 (0.2 µmol.L^{-1} Sn) in 3 d for exposure to bis(tributyltin) oxide, and 0.3 mg.L^{-1} (0.9 µmol.L^{-1} Sn) in 24 h and 0.15 mg.L^{-1} (0.4 µmol.L^{-1} Sn) in 3 d for tributyltin acetate. Plum (1981) recorded an LC_{50} value of 0.002 $mg.L^{-1}$ (7 $nmol.L^{-1}$ Sn) for *Daphnia magna* exposed to bis(tributyltin) oxide.

6.5.5 OTHERS

Two members of the crustacean class which are normally target organisms for organotin compounds are barnacles and gribbles. Trialkyltin compounds have a 0.1-1 $mg.L^{-1}$ activity range against barnacles (Evans and Smith 1975), one of the most common marine fouling species, although the exact mechanism by which these compounds exert their effect is not completely clear. Boulton *et al.* (1971) investigated the effect of concentrations of triethyltin sulfate lethal to the barnacle *Elminius modestus* after 30-36 h on the metabolism of glucose and acetate in order to determine the trialkyltin compound's mechanism of action. Some of the changes in metabolism observed could be attributed to a relative deficiency of ATP caused by an uncoupling action on oxidative phosphorylation; however, the extreme resistance of *Elminius* to the actions of the uncoupling agent 2,4-dinitrophenol suggested that triethyltin sulfate toxicity resulted from some other action. Other changes strongly suggested inhibition of pyruvate catabolism. Although triethyltin sulfate was found to be a noncompetitive inhibitor of pyruvate decarboxylase and lipoamide dehydrogenase, it did not inhibit these enzymes sufficiently to account for its toxicity. Boulton *et al.* (1971) suggested that the metabolic effects of triethyltin sulfate intoxication, implying a restriction of pyruvate utilization, resulted from an action on the dihydrolipoyl transacetylase component of pyruvate dehydrogenase.

Shi *et al.* (1981) found that the rates of oxidative phosphorylation in mitochondrial suspensions prepared from the cirrus muscle of the barnacle *Balanus amphitrite amphitrite* were significantly inhibited by triphenyltin chloride. Concentrations of triphenyltin chloride of 190 $\mu mol.L^{-1}$ inhibited respiration and phosphorylation by 54 and 100%, respectively, when sodium succinate was used as a substrate. An electron microscopic examination of the fine structure of the cirrus muscle mitochondria from the barnacle showed that triphenyltin chloride damaged the mitochondrial cristae.

Luijten (1972) noted that the adult gribble (*Limnoria*) was sensitive to organotin compounds, although less so than *Teredo* larvae (see Section 6.7.3.3). Vind and Hochman (1962a, b) assayed a large number of organotin compounds for their toxicity to the marine boring adult *Limnoria tripunctata*, finding that the di- and trisubstituted organotin compounds were particularly toxic when the substituents were ethyl, propyl, butyl, amyl and phenyl groups. An average of 0.8 $mg.L^{-1}$ Sn (7 $\mu mol.L^{-1}$ Sn) was required for a 50% kill, for the trialkyltin compounds tested.

6.6 ARTHROPODS - INSECTS

Organotin compounds are widely used as insecticides. Schaefer *et al.* (1981) treated a rice field paddy with enough triphenyltin hydroxide to give an average water concentration of 146 μg.L^{-1} triphenyltin hydroxide (0.4 μmol.L^{-1} Sn) 2 h after treatment; this treatment killed all populations of the larval mosquito *Culex tarsalis* and deerflies (*Chrysops* spp.). Mayflies, damselflies and chironomids were also affected.

The effects of organotin compounds on many species of insects have been reviewed by Ascher and Nissim (1964). In general, only trialkyl- and triaryltin compounds are truly insecticidal; the mono- and disubstituted compounds are relatively nontoxic. Blum and Pratt (1960) found evidence that organotin compounds may exert their toxic action as ions. It appears, then, that the toxicity is not greatly influenced by the nature of the anion, but instead is due to the presence of the three organic groups in a tetrahedral structure around the central tin atom (Ascher and Nissim 1964). For insects, the optimum alkyl chain length appears to be one carbon atom (i.e. trimethyltin compounds). Gardner and Poller (1964), on the other hand, found that the insecticidal activity of triphenyltin compounds was definitely dependent on the nature of the Q group.

Cardarelli (1978) examined the toxic effects of various dosages of materials containing tributyltin fluoride (daily release rate <10 μg.L^{-1}; <30 nmol.L^{-1} Sn) on mosquito (*Culex pipiens*) larvae over a 310-d exposure period. The organotin compound was found to be toxic to pupae at relatively low concentrations. Organotin compounds dramatically slowed or prevented morphogenesis, the normal egg-to-adult time of 8 or 9 d being extended to 21 or more days at sublethal levels. The lethal mechanism of organotin compounds for mosquitoes was not elucidated. Gras and Rioux (1965) determined the toxicities of various substituted organotin compounds against fourth stage *Culex pipiens* larvae, and found that the trialkyl- and triaryltin derivatives were most effective (average 24-h LC$_{50}$'s were 0.45 and 0.32 mg.L^{-1}, respectively).

Sherman and Hoang (1981) exposed third instar *Aedes aegypti* larvae to tributyltin fluoride. No larvae exposed to 100 or 200 μg.L^{-1} tributyltin fluoride (0.3 or 0.6 μmol.L^{-1} Sn) pupated; 12% of the larvae exposed to 20 μg.L^{-1} (0.6 nmol.L^{-1} Sn) pupated and became adults, but their development was greatly retarded. The authors speculated that this retardation of development indicated that protein synthesis inhibition is the toxic mechanism of action in mosquitoes.

Floch *et al.* (1964) calculated LC$_{100}$ values for dragonfly (*Aeschna*) larvae of 3 mg.L^{-1} (10 μmol.L^{-1} Sn) in 24 h and 0.25 mg.L^{-1} (0.84 μmol.L^{-1} Sn) in 48 h when the larvae were exposed to bis(tributyltin) oxide, and 4 mg.L^{-1} (11 μmol.L^{-1} Sn) in 24 h and 0.5 mg.L^{-1} (1.4 μmol.L^{-1} Sn) in 3 d for tributyltin acetate. *Notonectes* (back swimmers) exhibited LC_{100}'s of 2 $mg.L^{-1}$ (7 $\mu mol.L^{-1}$ Sn) in 24 h, 0.25 $mg.L^{-1}$ (0.84 $\mu mol.L^{-1}$ Sn) in 48 h and 0.06 $mg.L^{-1}$ (0.2 $\mu mol.L^{-1}$ Sn) in 3 d when exposed to bis(tributyltin) oxide, and 2 $mg.L^{-1}$ (6 $\mu mol.L^{-1}$ Sn) in 24 h and 0.15 $mg.L^{-1}$ (0.43 $\mu mol.L^{-1}$ Sn) in 3 d when they were exposed to tributyltin acetate. Chironomid larvae exposed to tributyltin acetate had LC_{100} values of 0.3 $mg.L^{-1}$ (0.9 $\mu mol.L^{-1}$ Sn) in 24 h and 0.15 $mg.L^{-1}$ (0.43 $\mu mol.L^{-1}$ Sn) in 48 h.

6.7 MOLLUSCS

6.7.1 INTRODUCTION

There is an abundance of literature available on the molluscicidal properties of organotin compounds, particularly their effects on snails, because several species of aquatic snails are intermediate hosts in the life cycles of certain parasitic worms that give man bilharziasis or schistosomiasis.

6.7.2 SNAILS

6.7.2.1 Toxicity

It is useful to examine the toxicity of organotin compounds towards aquatic snails, particularly since the snails will not always be target organisms for the actions of these compounds. The literature values for the toxicities of several triorganotin compounds to certain aquatic snails are compiled in Table 6-4. As was found with fish (see Section 6.4.1), several factors influence the toxicity of organotin compounds towards aquatic snails:

(i) Water Quality

Cardarelli and Evans (1980) found that certain aspects of water quality affected snail mortality in the presence of organotin compounds. For example, there was a marked dependence of the time required to kill 50 and 100% of the snails *Biomphalaria glabrata* and *Bulinus globosus* on pH for bis(tributyltin) oxide and tributyltin fluoride. Laughlin *et al*. (1982) discussed the influence of pH and the concentration of other ions present on the aqueous chemistry of trialkyltin compounds. The equilibrium mixture for bis(tributyltin) oxide, for example, is strongly affected by pH because its affinity for OH^- is greater than for Cl^-. This is important to bear in mind in examining the effects of organotin compounds on all aquatic organisms in natural situations, because different equilibrium proportions of trialkyltin compounds would be formed in estuaries or river mouths where pH and ionic strengths are less than in the open sea.

Table 6-4. The molluscicidal properties of certain trialkyltin compounds.

Compound	Species of snail	Lethal concentration			Comments	Reference
		Parameter	mg.L^{-1}	µmol.L^{-1} Sn		
Bis(tripropyltin) oxide	*Biomphalaria glabrata*	24-h LC$_{50}$	0.085	0.33	13-15 mm mature	Frick and de Jimenez (1964); Ritchie *et al.* (1964)
		24-h LC$_{90}$	0.115	0.45	13-15 mm mature	Frick and de Jimenez (1964); Ritchie *et al.* (1964)
		6-h LC$_{50}$	0.78	3.1	13-15 mm mature	Frick and de Jimenez (1964); Ritchie *et al.* (1964)
		6-h LC$_{90}$	1.05	4.2	13-15 mm mature	Frick and de Jimenez (1964); Ritchie *et al.* (1964)
		6-h LC$_{50}$	0.65	2.5		Seiffer and Schoof (1967)
		6-h LC$_{95}$	1.7	6.7		Seiffer and Schoof (1967)
		LC$_{50}$	0.28	1.1		Paulini (1964) (cited by Duncan 1980)
		24-h LC$_{50}$	0.05-0.1	0.2-0.41		Hopf *et al.* (1967)
Tripropyltin pentachlorophenate	*B. glabrata*	24-h LC$_{50}$	0.1-0.5	0.2-1		Hopf *et al.* (1967)
Tributyltin acetate	*B. sudanica*	LC$_{50}$	0.03	0.09		Webbe 1963 (cited by Duncan 1980)
	B. (P.) nasutus	LC$_{50}$	0.03	0.09		Webbe 1963 (cited by Duncan 1980)
	B. glabrata	24-h LC$_{50}$	0.085	0.24	13-15 mm mature	Frick and de Jimenez (1964); Ritchie *et al.* (1964)
		24-h LC$_{90}$	0.115	0.57	13-15 mm mature	Frick and de Jimenez (1964); Ritchie *et al.* (1964)
		6-h LC$_{50}$	0.19	0.55	13-15 mm mature	Frick and de Jimenez (1964); Ritchie *et al.* (1964)
		6-h LC$_{90}$	0.3	0.9	13-15 mm mature	Frick and de Jimenez (1964); Ritchie *et al.* (1964)
		24-h LC$_{100}$	0.30	0.90		Floch *et al.* (1964)
		LC$_{50}$	0.17	0.49		Paulini (1964) (cited by Duncan 1980)
		24-h LC$_{50}$	0.1-0.3	0.3-0.9		Hopf *et al.* (1967)
	B. contortus	24-h LC$_{100}$	0.30	0.90		Floch *et al.* (1964)
Tributyltin pentachlorophenate	*B. glabrata*	24-h LC$_{50}$	0.05-0.1	0.09-0.2		Hopf *et al.* (1967)
Bis(tributyltin) oxide	*B. tropicus*	LC$_{50}$	0.01	0.03		de Villiers and MacKenzie (1963) (cited by Duncan 1980)
	B. contortus	24-h LC$_{100}$	0.075	0.25		Floch *et al.* (1964); Deschiens and Floch (1968)
		24-h LC$_{50}$	0.03	0.1		Deschiens *et al.* (1966)
	B. glabrata	24-h LC$_{100}$	0.075	0.25		Floch *et al.* (1964); Deschiens and Floch (1968)
		24-h LC$_{50}$	0.03	0.1		Deschiens *et al.* (1966)
		24-h LC$_{50}$	0.05-0.1	0.2-0.3		Hopf *et al.* (1967)
		6-h LC$_{50}$	0.41	1.4		Seiffer and Schoof (1967)
		6-h LC$_{95}$	0.84	2.8		Seiffer and Schoof (1967)
		24-h LC$_{50}$	0.04	0.1		Ritchie *et al.* (1964)
		24-h LC$_{90}$	0.105	0.35		Ritchie *et al.* (1964)
		6-h LC$_{50}$	0.37	1.2		Ritchie *et al.* (1964)
		6-h LC$_{90}$	0.9	3		Ritchie *et al.* (1964)

Table 6-4. (Cont'd)

		Lethal concentration				
Compound	Species of snail	Parameter	mg.L^{-1}	μmol.L^{-1} Sn	Comments	Reference
Triphenyltin acetate	*B. glabrata*	24-h LC_{50}	0.05	0.1		Hopf and Muller (1962); Hopf *et al.* (1967)
		24-h LC_{100}	1.0	2.5		Deschiens and Floch (1962); Floch and Deschiens (1962)
		48-h LC_{100}	0.25	0.61		Deschiens and Floch (1962)
		24-h LC_{50}	0.66	1.6	13-15 mm mature	Frick and de Jimenez (1964); Ritchie *et al.* (1964)
		24-h LC_{90}	1.55	3.8	13-15 mm mature	Frick and de Jimenez (1964); Ritchie *et al.* (1964)
		LC_{50}	0.26	0.64		Paulini (1964) (cited by Duncan 1980)
		LC_{50}	0.50	1.2		Paulini (1964) (cited by Duncan 1980)
(20%)		6-h LC_{50}	0.4	0.2		Seiffer and Schoof (1967)
(20%)		6-h LC_{95}	1.4	0.69		Seiffer and Schoof (1967)
	B. contortus	24-h LC_{100}	1.00	2.5		Deschiens and Floch (1962); Floch and Deschiens (1962)
		48-h LC_{100}	0.25	0.61		Deschiens and Floch (1962)
	B. sudanica	LC_{50}	0.04	0.1		Webbe (1963) (cited by Duncan 1980)
	B. (P.) nasutus	LC_{50}	0.03	0.07		Webbe (1963) (cited by Duncan 1980)
	B. tropicus	LC_{50}	0.075	0.18		de Villiers and MacKenzie (1963) (cited by Duncan 1980)
Triphenyltin chloride	*B. glabrata*	24-h LC_{100}	1.00	2.7		Floch and Deschiens (1962); Deschiens and Floch (1962)
		48-h LC_{100}	0.25	0.68		Deschiens and Floch (1962)
		6-h LC_{50}	5.5	15		Seiffer and Schoof (1967)
		6-h LC_{95}	19.0	51		Seiffer and Schoof (1967)
	B. contortus	24-h LC_{100}	1.00	2.7		Floch and Deschiens (1962); Deschiens and Floch (1962)
		48-h LC_{100}	0.25	0.68		Deschiens and Floch (1962)
Triphenyltin fluoride	*B. glabrata*	24-h LC_{50}	0.01-0.05	0.03-0.1		Hopf *et al.* (1967)
Triphenyltin hydroxide	*B. tropicus*	LC_{50}	0.05	0.1		de Villiers and MacKenzie (1963) (cited by Duncan 1980)
		24-h LC_{50}	0.165	0.47		Ritchie *et al.* (1964)
		24-h LC_{90}	0.232	0.66		Ritchie *et al.* (1964)
		24-h LC_{50}	0.335	0.95		Ritchie *et al.* (1964)
		24-h LC_{90}	0.53	1.5		Ritchie *et al.* (1964)
Triphenyltin pentachlorophenate	*B. glabrata*	24-h LC_{50}	0.1-1.0	0.2-2		Hopf *et al.* (1967)
Tris-p-chlorophenyltin acetate	*B. glabrata*	24-h LC_{50}	0.01-0.05	0.02-0.1		Hopf *et al.* (1967)
Tris(2-phenylethyl)tin acetate	*B. glabrata*	24-h LC_{50}	0.01-0.05	0.02-0.1		Hopf *et al.* (1967)
Tribenzyltin pentachlorophenate	*B. glabrata*	24-h LC_{50}	1.0	1.5		Hopf *et al.* (1967)
Tri(cyclopentylmethyl)tin acetate	*B. glabrata*	24-h LC_{50}	0.05-0.1	0.1-0.2		Hopf *et al.* (1967)
Tricyclopentyltin acetate	*B. glabrata*	24-h LC_{50}	0.05-0.1	0.1-0.3		Hopf *et al.* (1967)
Tri-m-tolyltin acetate	*B. glabrata*	24-h LC_{50}	0.01-0.05	0.02-0.01		Hopf *et al.* (1967)
Tri-p-tolyltin acetate	*B. glabrata*	24-h LC_{50}	0.01-0.05	0.02-0.1		Hopf *et al.* (1967)

In addition, water hardness and presence of suspended organic materials (which the snails ingest during their browsing activities) are important (Cardarelli and Evans 1980). Walker (1977) found that the mortality of *B. glabrata* exposed to bis(tributyltin) oxide and tributyltin fluoride was a function of dosage and soil surface area, not of water volume. This suggested that the major transport mode for the organotin compounds was through the soil or soil/water interface (via ingestion) rather than through the water.

(ii) Concentration and Exposure Time

In general, it has been found that the longer the duration of exposure, the lower the concentration of organotin compound required to induce mortality (Ritchie *et al.* 1964; Berrios-Duran *et al.* 1968; van der Maas *et al.* 1972; Cardarelli 1974).

(iii) Structure of Compound

The molluscicidal activities of several heterocyclic organotin sulfide compounds R_3SnSR', where R' = heterocyclic grouping and R = alkyl, aryl, substituted aryl, vinyl, benzyl or cyclohexyl group, were determined by Ison *et al.* (1971). Overall, the nature of the R_3Sn grouping appeared to be the dominant factor controlling molluscicidal potencies, and the heterocyclic nucleus was only of secondary importance. For the trialkyl derivatives where R' = 2-pyridyl, the molluscicidal activities were dependent on the chain length of the alkyl group; they reached a maximum at C_4 and fell above C_7.

Ritchie *et al.* (1964) and Frick and de Jimenez (1964) found that molluscicidal activity was associated more with the propyl and butyl radicals than with the phenyl radical; Frick and de Jimenez (1964) determined the order of effectiveness against *B. glabrata* to be tributyltin acetate > bis(tripropyltin) oxide > triphenyltin acetate. Camey and Paulini (1964), on the other hand, found that toxicity decreased as follows: tributyltin acetate > triphenyltin acetate > bis(tripropyltin) oxide. This difference could be attributed to any of a number of procedural differences.

Smith *et al.* (1979) examined structure-activity relationships for several organotin molluscicides, and found little variation in the activities of tributyl- and triphenyltin compounds and mixed butyldiphenyltin compounds. Because it has been suggested that bis(tributyltin) oxide combines with certain amino acids in snail proteins, thereby destroying cell function (Cardarelli 1977; see Section 6.7.2.4), Smith *et al.* (1979) also investigated the effect of the Q group on molluscicidal activity using five-coordinated tributyltin compounds. The effect was observed to be minimal except for a compound containing an intramolecularly coordinated dialkylaminoethanol ligand, which presumably has a lower tendency to attack the active site(s) on the protein. The anionic group of the R_3SnQ molecule is therefore not directly involved in this pentacoordinate bonding; that would explain the anion independence of the biological activity of trialkyltin compounds (Rose 1971).

(iv) Size and Stage of Development

Frick and de Jimenez (1964) evaluated the molluscicidal properties of bis(tripropyltin) oxide, tributyltin acetate and triphenyltin acetate against B. glabrata eggs and hatched snails (<24 h, 3-5 mm adolescents, 8-10 mm juveniles, 13-15 mm mature) (Table 6-5). For the hatched snails, the concentration required to kill 50% of the snails tended to increase as the size of the target increased. The eggs incubated for 4 d, however, were less susceptible than all sizes of hatched snails. Similarly, Camey and Paulini (1964) found that susceptibility to tributyltin acetate, triphenyltin acetate and bis(tripropyltin) oxide decreased with the development of the snail B. glabrata; the mature snails were 5-10 times more resistant than the 5- to 15-h-old embryos.

6.7.2.2 Gross Behavioral and Pathological Changes

Frick and de Jimenez (1964) noted that B. glabrata snails exposed to lethal concentrations of bis(tripropyltin) oxide, tributyltin acetate or triphenyltin acetate developed an extended and much enlarged foot, a condition that persisted until death. Avoidance behavior of the snails was not pronounced, even at high concentrations. On the other hand, Seiffer and Schoof (1967) observed that snails crawled from solution at many concentrations of triorganotin compounds, and retracted at others. Allen et al. (1980) noted that snails exposed to 60 and 600 $\mu g.L^{-1}$ bis(tributyltin) oxide (active) (0.2 and 2 $\mu mol.L^{-1}$ Sn) ceased their browsing activity, lost their mobility, and underwent deep retraction.

Smith (1981a) observed that females of the common intertidal mud snail Nassarius obsoletus exhibited imposex, a condition whereby the female develops one or more of a penis, vas deferens, or convolution of a normally straight oviduct. This abnormality was first linked with pollution from marinas, then with antifouling paints containing triorganotin compounds as active ingredients (Smith 1981a). Smith (1981b) then showed that pure tributyltin compounds were capable of inducing imposex in mud snails, and demonstrated that there was a concentration-response relationship using bis(tributyltin) oxide, with a EC_{10} (10% effective concentration) for total and diagnostic frequency of 4.5-5.5 $\mu g.L^{-1}$ bis(tributyltin) oxide (15-19 $nmol.L^{-1}$ Sn) and an increase in response of the order of 2% per 1 $\mu g.L^{-1}$ increment of triorganotin compound (3 $nmol.L^{-1}$ Sn). Because there is no prominent decrease in reproductive capacity or alteration in population ecology

Table 6-5. Comparison of molluscicidal activity of three organotin compounds in 24-h exposures against representative stages and sizes of a laboratory strain of Puerto Rican B. glabrata (adapted from Frick and de Jimenez 1964)[α].

		Eggs					Adults			
		LC_{50}		LC_{90}			LC_{50}		LC_{90}	
Compound	Stage	mg.L^{-1}	µmol.L^{-1} Sn	mg.L^{-1}	µmol.L^{-1} Sn	Size (mm)	mg.L^{-1}	µmol.L^{-1} Sn	mg.L^{-1}	µmol.L^{-1} Sn
Tributyltin acetate	1-6 h[β]	0.031	0.089	0.072	0.21	3-5	0.041	0.12	0.056	0.16
	4 d[β]	0.23	0.66	0.45	1.3	8-10	0.074	0.21	0.105	0.30
	Newly hatched	0.019	0.055	0.041	0.12	13-15	0.086	0.25	0.115	0.33
Bis(tripropyltin) oxide	1-6 h[β]	0.06	0.24	0.117	0.46	3-5	0.029	0.11	0.033	0.13
	4 d[β]	0.099	0.39	0.17	0.67	8-10	0.043	0.17	0.078	0.31
	Newly hatched	0.03	0.12	0.049	0.19	13-15	0.085	0.33	0.115	0.45
Triphenyltin acetate	1-6 h[β]	0.12	0.29	0.22	0.54	3-5	0.305	0.75	0.44	1.1
	4 d[β]	1.6	3.9	3.5	8.6	8-10	0.65	1.6	0.84	2.1
	Newly hatched	0.07	0.17	0.155	0.38	13-15	0.66	1.6	1.55	3.8

[α] All concentrations expressed in milligrams of active ingredient per litre and micromoles of tin per litre.

[β] Incubation period before testing.

related to imposex, its occurrence can be used as a biological indicator of marine contamination with organotin compounds (Smith 1981b).

Shell thickening has been observed in the common pond snail (Limnaea stagnalis L.) exposed to low concentrations of trimethyl- and triethyltin chloride (10 $ng.L^{-1}$ - 1 $mg.L^{-1}$; ~0.05 $nmol.L^{-1}$ - 5 $\mu mol.L^{-1}$ Sn) (Buzinova and Danil'chenko 1984).

6.7.2.3 Cell/Tissue Changes

Snail tissue exposed to lethal and sublethal concentrations of bis(tributyltin) oxide exhibited massive cell wall destruction (Cardarelli and Evans 1980) and yellowish inclusions in connective tissue, black precipitates in epithelia (Patnode and Kanakkanatt 1971, cited by Duncan 1980), and loss of impermeability to hemolymph (Patnode and Kanakkanatt 1971, cited by Duncan 1980; Cardarelli and Evans 1980). Muscle and nerve tissue were less affected than gastrointestinal tissue (Cardarelli et al. 1969, cited by Allen et al. 1980; Patnode and Kanakkanatt 1971, cited by Duncan 1980).

Allen et al. (1980), noting that trialkyltin compounds react readily with amino acids and proteinaceous tissue, investigated the effects of bis(tributyltin) oxide on snail hemolymph protein. The bis(tributyltin) oxide accumulated in the hemolymph with a concentration proportional to the external bis(tributyltin) oxide concentration and exposure time. At all concentrations of the tributyltin compound, hemolymph protein levels decreased after initial exposure to bis(tributyltin) oxide; the authors suggested that this indicated that the compound combined quickly with specific hemolymph proteins of the snail. Subsequent increases in protein levels were attributed by the authors to a release of cellular proteins from damaged tissues or an attempt by the snail to replace specific proteins that had combined with bis(tributyltin) oxide.

There are two different types of cells in normal snail hemolymph - granulocytes and hyalinocytes. Short exposures to sublethal concentrations of bis(tributyltin) oxide caused no morphological changes in cells or inclusions. Although lethal doses caused the hemolymph to change color and consistency, this effect appeared to be caused by the snail's death, not by exposure to the organotin compound. The hemolymph cells (particularly granulocytes) of snails exposed to sublethal concentrations of bis(tributyltin) oxide showed an increase in the presence of phagocytized particles; however, because the hemolymph cell volume did not increase, Allen et al. (1980) concluded that the toxicant did not elicit an immunological response from the snails.

6.7.2.4 Biochemical Changes

Sharaf *et al.* (1974) found that triphenyltin hydroxide at its LC_{50} (0.34 and 0.16 $mg.L^{-1}$ (0.97 and 0.46 $\mu mol.L^{-1}$ Sn) for *Biomphalaria alexandria* and *Bulinus truncatus*, respectively) inhibited gluconeogenesis (by 50-60% in *B. truncatus* and 20-25% in *B. alexandria*), stimulated glycolysis, and markedly reduced glycogen content (by 58 and 74% in *B. alexandria* and *B. truncatus*, respectively) and glucose utilization in snail tissue preparations. The authors postulated that these *in vitro* biochemical effects, together with inhibition of oxidative phosphorylation (up to 50% inhibition for the oxidation of NAD-linked substrate), give rise to the *in vivo* molluscicidal activity of triphenyltin hydroxide.

The accumulation of bis(tributyltin) oxide in the mitochondrial fraction of snail tissue noted by Allen *et al.* (1980) suggests the possibility of inhibition of mitochondrial oxidation; electron microscopy indicates little if any morphological alteration in the mitochondria. Because histological studies on Ram's Horn snails (*Planorbis* spp.) have shown that bis(tributyltin) oxide combines with amino acids in proteinaceous tissue (report cited by Evans and Smith 1975), it has been postulated that trialkyltin compounds inhibit oxidative phosphorylation through a pentacoordinate binding of cysteine and histidine residues (Elliott *et al.* 1979). Binding to histidine in, for example, snail hemolymph, could also inhibit critical transamination processes (Allen *et al.* 1980). Dialkyltin species, the primary degradation product of trialkyltin compounds, react with sulfhydryl groups, possibly interfering with α-keto acid oxidation. The toxicity of these compounds towards snails is therefore probably due to their combination with proteins (Patnode and Kanakkanatt 1971, cited by Duncan 1980; Allen *et al.* 1980), although the sites of protein attachment and biochemical effects of such combinations are unknown (Allen *et al.* 1980).

Because of the apparent mechanism of toxicity (proteolysis, inhibition of transamination and oxidative phosphorylation), the development of resistance in snails to trialkyltin compounds is considered unlikely (Patnode and Kanakkanatt 1971, cited by Duncan 1980; Cardarelli and Evans 1980). In fact, when the parent snail generation has been exposed to sublethal dosages, a distinctive drop in tolerance of offspring generations has been observed, as well as dramatic changes in growth rate, fecundity and ova mortality (Cardarelli 1977). The accumulation of bis(tributyltin) oxide in snail reproductive tissue and nuclear material (see also Section 5.5.1.2) supports these studies which show a decrease in tolerance of successive generations to trialkyltin compounds (Allen *et al.* 1980).

6.7.2.5 Changes in Reproduction, Growth and Development

Ritchie *et al*. (1974) studied the effects of bis(tributyltin) oxide on oviposition, incubation and hatching of *Biomphalaria glabrata* eggs. Oviposition was completely inhibited by bis(tributyltin) oxide at 10 μg.L^{-1} (34 nmol.L^{-1} Sn), reduced by over 90% at 1 μg.L^{-1} (3.4 nmol.L^{-1} Sn) and by 50% at 0.1 μg.L^{-1} (0.34 nmol.L^{-1} Sn), and normal at 0.01 μg.L^{-1} (0.034 nmol.L^{-1} Sn). Development and hatching of eggs were also affected by prolonged exposure to bis(tributyltin) oxide (Ritchie *et al*. 1974). Newly laid eggs exposed to 10 μg.L^{-1} bis(tributyltin) oxide (34 nmol.L^{-1} Sn) did not develop. Only 3% of eggs hatched at 1 μg.L^{-1} (3.4 nmol.L^{-1} Sn), but 35% more hatched after a considerable delay when returned to water free from the triorganotin compound.

Other investigators have also found triorganotin compounds to interfere with the egg-laying and hatching processes. Cardarelli (1974) noted that oviposition and hatching were inhibited in *B. glabrata* exposed to bis(tributyltin) oxide (up to 0.035 mg.L^{-1}.d^{-1}; 0.12 μmol.L^{-1}.d^{-1} Sn) for 120 d. Deschiens and Floch (1968) found that bis(tributyltin) oxide was ovicidal at concentrations of 0.10 mg.L^{-1} (0.34 μmol.L^{-1} Sn) in 24 h. Triphenyltin chloride and acetate were shown to be ovicidal against egg laying by *B. glabrata* and the common pond snail, *Limnaea stagnalis*, at 1 mg.L^{-1} (≈2.6 μmol.L^{-1} Sn) in 24 h (Deschiens and Floch 1962).

Development of hatched snails can also be influenced by exposure to triorganotin compounds. Egg laying of snails exposed continuously to bis(tributyltin) oxide after hatching was significantly reduced in survivors at 1, 0.1, 0.01 and 0.001 μg.L^{-1} (3.4, 0.34, 0.034, and 0.0034 nmol.L^{-1} Sn), and growth was severely retarded at 1 and 0.1 μg.L^{-1} (3.4 and 0.34 nmol.L^{-1} Sn) (Ritchie *et al*. 1974). van der Maas *et al*. (1972) reported decreased production of eggs per deposited capsule and growth retardation in *Lymnaea stagnalis*, even at 0.002 mg.L^{-1} triphenyltin hydroxide (6 nmol.L^{-1} Sn).

6.7.3 PELECYPODS

6.7.3.1 Clams

Good *et al*. (1980) examined the effects of tributyltin acetate on the invertebrate filter-feeding clams *Rangia cuneata* from a south Louisiana estuary. At 0.02 mg.L^{-1} tributyltin acetate (57 nmol.L^{-1} Sn), all adult clams (3-6 cm in length) survived the length of the experiment (17 d); at 0.10 mg.L^{-1} (0.29 μmol.L^{-1} Sn), clams survived for at least 8 d; and at 1.0 mg.L^{-1} (2.9 μmol.L^{-1} Sn), all clams died within 5 d. The clams exhibited several distress symptoms a few hours after exposure to tributyltin acetate, including (i) low protrusion of siphons from shells; (ii) excess mucus release; (iii) swollen and rubbery siphons and mantle edges; and (iv) insensitivity to touch. Death occurred whether the valves were open or closed.

The lethal concentration for juvenile *Rangia cuneata* exposed to tributyltin acetate was below 0.02 mg.L^{-1} (57 nmol.L^{-1} Sn); all clams died within 20 d. The distress symptoms exhibited by these juveniles were similar to those for adult *Rangia cuneata*.

6.7.3.2 Oysters and Mussels

His and Robert (1980) studied the influence of tributyltin acetate on embryogenesis and larval development in the Japanese oyster, *Crassostrea gigas*. They observed that fertilization was completely inhibited at 100 μg.L^{-1} tributyltin acetate (0.29 μmol.L^{-1} Sn) after 24 h, egg cleavage was inhibited by 20% at 10 μg.L^{-1} (29 nmol.L^{-1} Sn), and 100% of the eggs at 5 μg.L^{-1} (14 nmol.L^{-1} Sn) yielded grossly abnormal trochophores. They also found that D larvae were highly sensitive to the presence of tributyltin acetate; after a 24-h exposure to 5 μg.L^{-1} tributyltin acetate (14 nmol.L^{-1} Sn), 30% of the larvae died, 8% exhibited morphological abnormalities, and most swam in an abnormal pattern. A 48-h exposure to 5 μg.L^{-1} (14 nmol.L^{-1} Sn) caused 100% mortality. His *et al.* (1983) suggested that current chemical methods are not sensitive enough to measure concentrations of tributyltin acetate at the toxicity limits of oyster larvae in seawater. They therefore compiled a table of effects of this compound at concentrations between 0.02 and 100 μg.L^{-1} (0.06 nmol.L^{-1} - 0.29 μmol.L^{-1}) on *Crassostrea gigas* veligers, and suggested these biological effects be used to determine the concentrations of tributyltin acetate in seawater.

The effects of tributyltin acetate on Japanese oyster and mussel (*Mytilus galloprovincialis*) larvae were compared by Robert and His (1981). They found that at 1 μg.L^{-1} (3 nmol.L^{-1} Sn), all *C. gigas* D larvae formed were abnormal and smaller in size than controls, whereas only 50% of the mussel D larvae formed were abnormal, an indication that the mussel veligers were much less sensitive to the effects of the pollutant. The growth of D larvae was severely affected for both species at 1 μg.L^{-1} (3 nmol.L^{-1} Sn). The mortality of *C. gigas* D larvae was 100% after a 12-d exposure to 1 μg.L^{-1} (3 nmol.L^{-1} Sn) and a 7-d exposure to 3 μg.L^{-1} (9 nmol.L^{-1} Sn). *Mytilus galloprovincialis* D larvae experienced 6% mortality after a 10-d exposure to 1 μg.L^{-1} (3 nmol.L^{-1} Sn) and 25% after a 9-d exposure to 3 μg.L^{-1} (9 nmol.L^{-1} Sn).

Alzieu *et al.* (1980) found 30% mortality in adult oysters exposed to 0.2 μg.L^{-1} tributyltin species for 113 d, and 100% mortality in those exposed to 2 μg.L^{-1} for 30 d. Thain (1983) examined the toxicity of bis(tributyltin) oxide to *Crassostrea gigas* and the European flat oyster, *Ostrea edulis*, as well as to the mussel, *Mytilus edulis*, and found that the larvae were much more sensitive than the adults. For example, 48-h LC$_{50}$ values for *Crassostrea gigas* were 1800 (adult) and 1.6 (larvae) μg.L^{-1} (6000 and 5.4 nmol.L^{-1} Sn), and those for *Mytilus edulis* were 300 (adult) and 2.3 (larvae) μg.L^{-1} (1000 and 7.7 nmol.L^{-1} Sn). The author speculated that the adults were more resistant because they can reduce their exposure to the organotin compound by closing their valves. These studies all indicate the acute and chronic toxicity of tributyltin compounds towards oyster and mussel embryos, larvae and adults.

Farming of the marine oyster *Crassostrea gigas* has been impeded in recent years by the development of abnormally weak larvae which are unable to attach to collectors and by the emergence of shell deformities consisting of chambers containing gelatinous material. His and Robert (1981a, cited by Alzieu *et al.* 1980) attributed the degeneration of the larvae to substances *in the* water that (i) acted on embryo development by interfering with certain biosynthetic processes, resulting in abnormal biochemical composition in the larvae, or (ii) directly affected the development of specific nanoplankton required by the D larvae during the first few days of their pelagic existence.

Alzieu *et al.* (1980, 1982) and Héral *et al.* (1981, cited by Alzieu *et al.* 1980) examined the shell deformities in *C. gigas*, and found that the degree of abnormal calcification was related to the proximity to pleasure or commercial boating activities. Alzieu *et al.* (1982) then examined the development of abnormal calcification in the presence of antifouling paints that leached organotin compounds. They noted that these organotin derivatives were indeed capable of causing abnormalities similar to those observed in oyster beds.

Alzieu *et al.* (1982) speculated on the mechanism of disruption of the oyster calcification process by organotin compounds. That disruption causes the shell to become lamellar in structure and to contain pockets of jelly-like material. The oyster's exoskeleton consists of a mineral fraction (calcium and magnesium salts) embedded in an organic matrix (proteins and glycoprotein). The organotin compounds could therefore disrupt calcification by (i) inhibiting calcium carbonate crystallization, either by blocking the synthesis of ATP required for the crystallization or by causing changes in levels of zinc, an essential component of carbonic anhydrase, or (ii) acting on the synthesis of the organic matrix, by complexing with amino acids and causing the secretion of a protein jelly which is unsuitable for calcium fixation. Krampitz (1980, personal communication to Alzieu *et al.* 1980) determined that the amino acid serine, which ensures calcium fixation in the calcification protein, does not occur in the abnormal jelly; instead, the jelly is rich in threonine which is incapable of fixing Ca^{2+}.

Recent experiments by Waldock and Thain (1983) have confirmed the observations by Alzieu *et al.* (1980, 1982) of shell thickening in *Crassostrea gigas* exposed to low concentrations of tributyltin compounds. Spat cultured in 0.15 $\mu g.L^{-1}$ bis(tributyltin) oxide (0.51 $nmol.L^{-1}$ Sn) for 56 d grew less well than the controls and showed pronounced thickening of the upper shell valve; the formation of proteinaceous gel was not noted. High levels of toxicant (1.6 $\mu g.L^{-1}$; 5.4 $nmol.L^{-1}$ Sn) severely inhibited oyster growth. Mortalities in these growth experiments were extremely low.

6.7.3.3 Shipworms

Vind and Hochman (1962a, b) examined the toxicity of organotin compounds to the marine boring Teredo diegensis (shipworm) larvae. Trisubstituted organotin compounds were a little more toxic than disubstituted organotin compounds, particularly those whose substituents were ethyl, propyl, butyl, amyl and phenyl groups (<0.05 mg.L^{-1} minimum concentration to kill Teredo larvae). Larger and smaller (methyl) alkyl substituents were much less toxic, as were tetrasubstituted organotin compounds. The nature of the anionic radical had little influence on the toxicity of the organotin compounds to the Teredo larvae.

6.8 HIGHER PLANTS

The interactions between organotin compounds and higher plants should be of major concern because of potential effects on primary productivity. However, little information is available in this area, and what studies have been performed concern terrestrial rather than aquatic plants.

The major effect of triorganotin compounds on plants that has been observed is interference with chloroplast functions through inhibition of photophosphorylation reactions by acting as uncouplers, and inhibition of electron transport (Kahn 1968; Watling and Selwyn 1972; Watling-Payne and Selwyn 1974; Gould 1976) in pea (Pisum sativum) and spinach (Spinacia oleracia). It can only be assumed that these effects could also occur in aquatic plants. Since organotin compounds inhibit mitochondrial respiration in animal systems (see, for example, Aldridge and Street 1970, 1971), they could possibly act in a similar manner in aquatic plant systems.

6.9 ALGAE

Little is known about the effects of organotin compounds on aquatic algae. However, as with higher plants, such interactions should be of major concern because of potential effects on primary productivity.

Tributyl- and triphenyltin compounds are effective against algae (Evans and Smith 1975; Phillip 1975). Different species of algae vary considerably in their sensitivity to the same organotin compound. Thain (1983) found an enormous difference in sensitivity of Tetraselmis suecica, a green, unicellular flagellate, and Skeletonema costatum, a diatom, to bis(tributyltin) oxide, with concentrations of 560-1000 µg.L^{-1} (1900-3400 nmol.L^{-1} Sn) and 1-18 µg.L^{-1} (3.4-60 nmol.L^{-1} Sn) being algistatic to the two species tested, respectively, within 5 d, and higher concentrations being algicidal.

An unspecified *Enteromorpha* was inhibited by a tributyltin fluoride antifouling paint that leached tin at a rate of about 0.07 μmol.cm^{-2}.d^{-1}. In contrast, the barnacle *Balanus balanus* was inhibited at a rate of about 0.03 μmol Sn.cm^{-2}.d^{-1} (de la Court 1977), indicating that barnacles may be more sensitive than organisms that precede them in the fouling sequence.

Spores of *Enteromorpha intestinalis* and *Ulothrix flacca* were exposed to triphenyltin chloride. Respiratory oxygen uptake was inhibited to similar degrees in each organism, but photosynthetic oxygen evolution was greater in *E. intestinalis* than in *U. flacca* (Callow *et al.* 1979).

Photophosphorylation was inhibited (0.02 μmol.L^{-1} tributyltin chloride) in chloroplasts from the alga *Euglena gracilis*. Electron transport was not inhibited. It was suggested that the tributyltin moiety binds to chloroplasts close to or at the site where the coupling factor binds (Kahn 1968).

Axenic cultures of *Scenedesmus quadricauda*, *Ankistrodesmus falcatus*, and *Anabaena flos-aquae* were examined for sensitivity to 11 tin compounds. Trialkyltin compounds were more effective than inorganic Sn(II) or Sn(IV), or mono- or disubstituted organotin compounds. Among trialkyltin compounds, the butyl- and phenyltin species were most effective: algal reproduction was inhibited 50% at 0.002-0.005 mg.L^{-1} (≈6-16 nmol.L^{-1} Sn) while primary productivity was less sensitive, being inhibited 50% at 0.01-0.04 mg.L^{-1} (≈30-140 nmol.L^{-1} Sn). Mixed natural phytoplankton from Lake Ontario showed 50% inhibition of primary productivity at 0.002-0.003 mg.L^{-1} (≈6-10 nmol.L^{-1} Sn) by tributyl- and triphenyltin species (Wong *et al.* 1982). Among trialkyltin compounds there was a relationship between the octanol:water partition coefficient and toxicity for primary productivity of *A. falcatus*: the more lipophilic the trialkyltin compound, the more toxic it was. The relationship did not apply to other tin compounds (Chau and Wong 1981; Wong *et al.* 1982).

6.10 FUNGI

Organotin compounds are used widely as fungicides, being active against representatives of Phycomycetes, Ascomycetes, Basidiomycetes, and the Fungi Imperfecti. Reviews are available (Ingham *et al.* 1960; Kaars Sijpesteijn *et al.* 1969; Luijten 1972).

In general, trialkyltin compounds of the type R_3SnQ are active against fungi. R may be the same group or different groups, and maximum toxicity occurs when there are 9 to 12 total carbons in the three alkyl groups. Q may be a halogen, hydroxyl, carboxyl, oxygen, or acetate. The nature of Q does not seem to influence toxicity except by altering solubility or by limiting dissociation to the presumed toxic forms R_3SnOH and R_3Sn^+. It has been suggested, for example, that in cases where the anionic radical results in the formation of a polymeric structure or a five-coordinated chelated monomer, a significant reduction in activity may occur (Blunden *et al.* 1984a). Disubstituted alkyltin compounds are markedly less *toxic to* fungi - usually by a factor of a hundred - than are trisubstituted compounds (van der Kerk and Luijten 1954, 1955, 1956; Nishimoto and Fuse 1966; Kaars Sijpesteijn *et al.* 1969).

Tripropyl- and tributyltin acetates are active at 1 mg.L^{-1} or less (≈3 µmol.L^{-1} Sn) (van der Kerk and Luijten 1954; Kaars Sijpesteijn *et al.* 1962). Tri-iso-alkyltin compounds are as effective as compounds *containing* normal isomers (van der Kerk and Luijten 1954). Introduction of a functional group, especially hydrophilic groups, reduces antifungal activity (Noltes *et al.* 1961). Among trisubstituted acetate derivatives, *triphenyltin* compounds were more effective against fungi than were the tri-m-tolyl, tri-p-tolyl, tribenzyl, tris-2-phenylethyl, or tri-α-naphthyl derivatives (Luijten and van der Kerk 1961). Di- and tetrasubstituted compounds showed little activity, except for diphenyltin dichloride which inhibited four test organisms at 10-20 mg.L^{-1} (29-58 µmol.L^{-1} Sn) (Kaars Sijpesteijn *et al.* 1969).

A number of phytopathogenic and obligately parasitic fungi have been examined for susceptibility to organotin compounds. Much of this work has been summarized by Kaars Sijpesteijn *et al.* (1969). Tripropyl-, tributyl-, and in some cases triethyl*substituted* compounds are effective in the range of 0.1-1 mg.L^{-1} (≈0.3-3 µmol.L^{-1} Sn). Other trisubstituted compounds were less effective, except for triphenyltin acetate, which was effective at 0.3-1 mg.L^{-1} (0.8-2.5 µmol.L^{-1} Sn) against three phytopathogens. Diphenyltin dichloride was the most effective of 18 organotin compounds tested for controlling *Colletotrichum falcatum*, the etiologic agent of wet rot disease on sugar cane. *Fungitoxic activity* was increased by formation of a diphenyltin dichloride-2,2-bipyridyl complex or a diphenyltin dichloride-1,10-phenanthroline complex (Srivastava *et al.* 1972). When applied to green bean plants at 20 or 100 mg.L^{-1} (68 or 340 µmol.L^{-1} Sn) 48 h after inoculation, dicyclohexylphenyltin hydroxide was more effective than triphenyltin hydroxide in controlling *Erisiphe polygoni*, the pathogen of powdery mildew (Gitlitz 1975).

As with bacteria, the medium can influence the sensitivity of fungi to organotin compounds. Lancashire and Griffiths (1975) examined 60 strains of *Saccharomyces cereviseae* for sensitivity to triethyltin species. In *all cases growth on glycerol* medium was inhibited by 1-2 µmol.L^{-1} triethyltin species, while on glucose medium 80-160 µmol.L^{-1} triethyltin species was required for inhibition. One strain, D22, was more sensitive on ethanol medium than on glucose medium. Strains resistant to triethyltin compounds were also resistant to other trialkyltin compounds, including methyl, propyl, butyl, phenyl, and cyclohexyl derivatives.

Yamada et al. (1978) screened four trisubstituted alkyltin compounds against eight fungi. Tributyltin species inhibited growth at 0.5-4 $mg.L^{-1}$ (0.2-13 $\mu mol.L^{-1}$ Sn), and tripropyltin species inhibited at 2-6 $mg.L^{-1}$ (8-23 $\mu mol.L^{-1}$ Sn); in one case triethyltin species were active at 3 $mg.L^{-1}$ (13 $\mu mol.L^{-1}$ Sn). The effectiveness of tripropyltin species on the yeast Saccharomyces cereviseae was influenced by pH and by the growth stage of the culture. Carraher et al. (1979) examined the antifungal activity of polyethyleneimines containing organotin moieties. Samples of polymer containing triphenyltin species inhibited three test fungi, but the minimum inhibitory concentration (MIC) was not given.

Mutants of S. cereviseae resistant to triethyltin sulfate can be grouped into two classes: (1) those that are also resistant to a variety of inhibitors and uncoupling agents that affect mitochondrial membranes, and (2) those that are also resistant to the uncoupling agent, bis(hexafluoroacetonyl) acetone. Mutations involved in class 1 are under the control of nuclear genes and those involved in class 2 are under the control of cytoplasmic (mitochondrial) genes. Recombination studies indicated that mutations to triethyltin resistance were not allelic with mutations to oligomycin resistance; thus, the triethyltin binding site involves a different gene product than the oligomycin-binding gene product(s) (Lancashire and Griffiths 1975).

Dibutylchloromethyltin chloride and dibutyltin dichloride are potent inhibitors of yeast mitochondrial ATPase by reaction with lipoic acid. Dibutyltin species also inhibit substrate level phosphorylation by reacting with dihydrolipoate associated with pyruvate dehydrogenase and α-ketoglutarate dehydrogenase (Cain et al. 1977). Adenosine triphosphatase in cell-free extracts of the yeast Schizosaccharomyces pombe was inhibited by triethyltin sulfate and by dibutylchloromethyltin chloride. It was suggested that the two tin compounds inhibited the F component of the ATP synthase complex, as did oligomycin and venturicidin (Lloyd and Edwards 1977).

Thus, organotin compounds appear to inhibit energy-yielding biochemical reactions in fungi, as they do in animals. Triethyltin bromide inactivates yeast hexokinase B. The inactivation is temperature-dependent since it did not occur at 20°C or lower. Triethyltin species induced a conformational change in the enzyme which was prevented by glucose. The enzyme is a dimer, and each monomer contains two sites of different affinity for the triethyltin moiety. Binding of the triethyltin moiety favored dissociation of the dimer, and inactivation was associated with a later event. Among five organotin compounds examined, effectiveness as an inhibitor was related to increasing hydrophobicity of the alkyl groups; thus, the tributyltin species was more potent than the triethyltin species (Siebenlist and Taketa 1983a). Binding of triethyltin bromide to the enzyme changes the reactivity of sulfhydryl groups. Neither cysteine nor histidine appears to be a donor ligand for the tin compound (Siebenlist and Taketa 1983b).

6.11 BACTERIA

In a review, Luijten (1972) stated that organotin compounds are more effective against Gram-positive organisms, often inhibiting growth at concentrations as low as 0.1-5 mg.L^{-1}, than against Gram-negative organisms, where concentrations of 20-50 mg.L^{-1} are required.

Bis(tributyltin) oxide mixed in a paper pulp substrate killed *Bacillus mycoides*, *Aerobacter aerogenes*, and *Pseudomonas aeruginosa* at concentrations of <10, 500, and >500 mg.L^{-1} (<33, 1600, >1600 μmol.L^{-1} Sn), respectively. Bis(tripropyltin) oxide was more effective; it was bactericidal at 1, 100, and 500 mg.L^{-1} (3.8, 380, 1900 μmol.L^{-1} Sn), respectively (Zedler and Beiter 1962). Kaars Sijpesteijn *et al.* (1962) screened 10 trisubstituted organotin compounds for effectiveness against four bacteria. Compounds with 9 (tripropyltin) through 15 (tripentyltin) carbon atoms were most effective against the Gram-positive organisms *Bacillus subtilis* (minimum inhibitory concentration (MIC) 2-5 mg.L^{-1}; 5.4-18 μmol.L^{-1} Sn) and *Mycobacterium phlei* (MIC 0.1-0.2 mg.L^{-1}; 0.27-0.7 μmol.L^{-1} Sn). Against the Gram-negative organisms *Escherichia coli* and *Pseudomonas fluorescens*, triethyl-, tripropyl-, and triisopropyltin compounds were most effective (MIC 20-50 mg.L^{-1}; 82-175 μmol.L^{-1} Sn). Grün and Fricker (1963) reported that tributyltin benzoate at 2 mg.L^{-1} (4.8 μmol.L^{-1} Sn) inhibited *Staphylococcus aureus* but 500 mg.L^{-1} (1.2 mmol.L^{-1} Sn) was required to inhibit each of three Gram-negative bacteria. Against *E. coli*, bis(tributyltin) oxide was more effective than any of three other tributyltin derivatives, and each of four tripropyltin derivatives was more effective than the tributyltin compounds. Kaars Sijpesteijn *et al.* (1969) screened 14 di- and trisubstituted organotin compounds for effectiveness against *Streptococcus lortis*. The tripropyl-, tributyl- and tricyclohexyltin compounds were the most toxic, inhibiting growth at 5 mg.L^{-1} (≈9.5-10.5 μmol.L^{-1} Sn). In both di- and trisubstituted series, toxicity increased in the order methyl < ethyl < propyl = butyl; further increases in alkyl chain length decreased toxicity: pentyl > hexyl. Disubstituted methyl and ethyl compounds were more effective than their trisubstituted homologues, but trisubstituted compounds were more effective than disubstituted among the propyl, butyl, pentyl, hexyl and cyclohexyl pairs. Yamada *et al.* (1978) determined the MIC of trimethyl-, triethyl-, tripropyl and tributyltin chlorides against eight bacteria. For most of the organisms tripropyltin chloride was the most toxic (MIC ranged from 5 to 100 mg.L^{-1}; 18-350 μmol.L^{-1} Sn), in four cases tributyltin chloride was equally strong, and for three organisms triethyltin chloride was more effective than tributyltin chloride. The toxicity of tripropyltin chloride to the bacteria *Escherichia coli* and *Bacillus subtilis* and the yeast *Saccharomyces cereviseae* was affected by the growth stage of the organisms, the pH of the growth medium, and the presence of surface-active agents.

The MIC of diethyltin species in agar medium against *E. coli* was 1.4 mg.L^{-1} (0.04 mmol.L^{-1} Sn) in a glucose-mineral salts agar, but when peptone or casamino acid was added to the medium the MIC was 14 $mg.L^{-1}$ (0.4 $mmol.L^{-1}$ Sn) (Kahana and Kaars Sijpesteijn 1967). Concentrations of tin as low as 5 $mg.L^{-1}$ (14 $\mu mol.L^{-1}$) as $SnCl_4.5H_2O$ inhibited mixed microbial flora from Chesapeake Bay. When sediment samples were plated on media containing either 75 $mg.L^{-1}$ (0.2 $mmol.L^{-1}$) Sn as $SnCl_4$ or 15 $mg.L^{-1}$ (69 $\mu mol.L^{-1}$) Sn as dimethyltin species, the dimethyltin compound was more toxic than inorganic tin (Hallas and Cooney 1981a). Substitution of gelatin or silica gel for agar as the solidifying agent in plating media decreased the apparent toxicity of $SnCl_4$ (Hallas and Cooney 1981a; Hallas *et al.* 1982b), as did humic acid or gelatin when it was added to medium solidified with agar (Hallas *et al.* 1982b). Addition of the sulfhydryl amino acid cysteine did not affect the toxicity of $SnCl_4$, but hydroxyflavone, which has hydroxy and keto functions, or serine, which has a hydroxy functional group, increased toxicity. Thus, compounds that can complex with tin can alter its toxicity, and one should use caution in attempting to extrapolate data on toxicity obtained by plating microorganisms on media from the laboratory to the environment.

Hallas and Cooney (1981b) determined the MIC for $SnCl_4$ and 18 organotin compounds against pure cultures of a yeast and 10 bacteria isolated from Chesapeake Bay. Di- and trisubstituted compounds were most effective, and ethyl, propyl, and butyl substituents were the most toxic, although there was variation in sensitivity patterns among the organisms. In many cases trisubstituted and sometimes disubstituted compounds were effective at tin concentrations of less than 1 $mg.L^{-1}$ (8 $\mu mol.L^{-1}$ Sn).

Tripropyltin chloride at concentrations as low as 10 $\mu g.mL^{-1}$ (35 $\mu mol.L^{-1}$ Sn) caused leakage of cellular material from and lysis of *E. coli* and *Bacillus subtilis* (Yamada *et al.* 1979a). While adsorption of tin to cells was independent of temperature (Yamada *et al.* 1978), leakage and lysis occurred at 30°C but not at 0, 60, or 100°C. Divalent cations, but not monovalent cations, inhibited both adsorption (Yamada *et al.* 1978) and leakage (Yamada *et al.* 1979a) of cellular materials. Yamada *et al.* (1979b) showed that KH_2PO_4 reversed inhibition of growth of *E. coli* by tripropyltin chloride. The membrane phospholipids, phosphatidyl ethanolamine and phosphatidyl serine, each formed a complex with tripropyltin chloride. Yamada and Watanabe (1979a) found that tripropyltin chloride did not inhibit oxygen consumption by *E. coli* at concentrations that inhibited growth. Protein, DNA, and RNA syntheses, as well as membrane-bound ATPase, were inhibited. Yamada and Watanabe (1979b) examined the effect of tripropyltin chloride on transport systems in *E. coli*. Uptake of L-leucine and of adenine was completely inhibited by tripropyltin chloride, and L-proline uptake was inhibited to a lesser degree. Tripropyltin chloride did not inhibit adenine uptake or the activity of leucine binding protein.

Soracco and Pope (1983) examined the effects of tributyltin oxide on *Legionella pneumophila*. There was a significant correlation between dose and cellular responses. Bacteriostasis occurred at about

10^7 molecules per cell and was characterized by an immediate decrease in adenylate energy charge and in intracellular ATP; after a 30-min exposure, RNA and protein syntheses were affected followed by inhibition of DNA synthesis and oxidation functions. Cells remained viable for at least 5 h. At higher, bactericidal concentrations ($>10^7$ molecules per cell), 90% of the cells lost viability within 1 min.

At 27 $mg.L^{-1}$ (0.08 $mmol.L^{-1}$ Sn), a concentration below the MIC for growth on a rich medium, diethyltin species inhibited oxygen uptake by E. coli with glucose, lactate, pyruvate or glutamate as substrate. With glucose or lactate, inhibition of oxygen uptake was accompanied by an increase in pyruvic acid accumulation. With glutamate as substrate, α-keto acid production was inhibited. Under anaerobic conditions, production of ethanol, carbon dioxide and hydrogen was inhibited. It was suggested that inhibition of pyruvate metabolism resulted in a lack of acetyl-CoA (Kahana and Kaars Sijpesteijn 1967). This is consistent with inhibition of lipoic acid in mitochondria reported for other organotin compounds in higher organisms (Cain et al. 1977).

Tributyltin species increased anion permeability in lipid bilayers (Tosteson and Wieth 1979). At concentrations that inhibited growth of E. coli, tributyltin compounds inhibited uptake of glutamine and proline and caused leakage of amino acids that had been accumulated. These compounds dissipated a pH gradient in cells and in everted membrane vesicles, leading to the conclusion that they catalyze a transmembrane hydroxyl ion-anion exchange reaction (Singh and Bragg 1979a). They appear to react with a sulfhydryl group(s) on a $NADP^+$-NADH transhydrogenation system, thus inhibiting respiration and the ATP-dependent transhydrogenation (Singh and Bragg 1979b).

Mukohata and Kaji (1981) examined the effects of triphenyltin compounds and other inhibitors on the light-dependent activities of Halobacterium rubrum. Triphenyltin compounds had a negligible effect on ATP synthesis in the light and in the dark, but they inhibited light-induced proton uptake and partly inhibited membrane potential. It was postulated that the triphenyltin species acted as a chloride/hydroxide exchanger.

Blair et al. (1982) observed that tributyltin cation bound to cells of tin-resistant estuarine bacteria, probably to the cell envelope. Jonas and Cooney (1983) noted that estuarine organisms resistant to dimethyltin species did not accumulate it, but that killed cells or starved (but viable) cells accumulated tributyltin compounds and stannic chloride rapidly. These observations are consistent with the suggestion that resistance to tin compounds may be by passive binding in or on the cell envelope, and by exclusion of the toxic compound from the cell.

7.0 PREDICTIONS OF EFFECTS FROM OBSERVED LEVELS

Tabulations of toxicant dose-effect data are useless unless an attempt is made to correlate the experimental data with observed levels of pollutant in the environment. This chapter will correlate available data or define what information needs to be gathered before such an assessment can be made.

As was noted in Section 5.2, methyltin compounds, which can be derived from anthropogenic sources as well as from biotic and abiotic methylation of inorganic tin and organotin compounds, have been found in a variety of natural waters. Concentrations of methyltin species in fresh water in Canada range from 0.5 to 10 nmol.L^{-1} Sn for $MeSn^{3+}$ (n=28); 0.17 to 3.4 nmol.L^{-1} Sn for Me_2Sn^{2+} (n=28); and 0.42 nmol.L^{-1} Sn for Me_3Sn^+ (n=1) (see Table 5-4). In marine and estuarine waters (e.g. Florida coast, San Diego Bay, Chesapeake Bay), concentrations range from <0.084 to 353 pmol.L^{-1} Sn for $MeSn^{3+}$ (n=4); 5.04 to 4120 pmol.L^{-1} Sn for Me_2Sn^{2+} (n=5); <0.084 to 168 pmol.L^{-1} Sn for Me_3Sn^+ (n=3); and <0.084 to 2.52 nmol.L^{-1} Sn for Me_4Sn (n=1) (see Table V-1 in Appendix V.0). No measurements have been made of concentrations of organotin compounds in Canadian marine and estuarine waters.

Although there are many aquatic data on the occurrence of methyltin species in aquatic environments, few measurements of the effects of these species on aquatic organisms have been reported because they are thought to be only slightly toxic. It is therefore not possible to draw any conclusions regarding the effects of observed levels of methyltin compounds on aquatic organisms in Canadian waters; experimental measurements of the effects of long-term exposures to low levels of these compounds, alone and in combination with other pollutants and stresses, in both freshwater and marine environments, are necessary before such correlations can be made.

Butyltin compounds, which are usually detected in and around harbor locations because of their anthropogenic sources, have been measured only in fresh water. Concentrations of butyltin species in unfiltered subsurface fresh water (from harbor locations) range from 0.035 to 10 nmol.L^{-1} Sn for Bu_3Sn^+ (n=8); 0.043 to 31 nmol.L^{-1} Sn for Bu_2Sn^{2+} (n=20); and 0.11 to 48 nmol.L^{-1} Sn for $BuSn^{3+}$ (n=2) (see Table 5-2). In contrast to the toxicity data available for methyltin compounds, there is an abundance of information on the effects of the more toxic butyltin compounds (i.e. tributyltin species) on aquatic organisms. We shall therefore concentrate our efforts on predicting the effects of tributyltin compounds on aquatic organisms in Canadian waters as a result of observed levels of these organotin compounds.

It should be pointed out that the experiments of primary interest are those of long-term exposures to relatively low concentrations of toxicant. Many researchers have calculated short-term (e.g. 24-h or 48-h) lethal concentrations for aquatic organisms; for example, the 24-h LC_{50} for fish exposed to triphenyl- and tributyltin compounds can be roughly estimated to be between 0.03 and 0.5 $mg.L^{-1}$ (≈90-1700 $nmol.L^{-1}$ Sn) (see Table 6-1). However, these concentrations far exceed those found in Canadian natural waters, and as a result no predictions can be made concerning the effects on Canadian fish. Although more and more researchers are performing chronic exposure experiments, there is still not enough information available at the present time to make any definitive statements regarding the concentration-effect relationship with time.

It should also be emphasized that it is not sufficient to extrapolate the results of short-term experiments using low concentrations of toxicant, because the processes of metabolism, clearance and bioconcentration play an important role in determining the toxic effect of the compound. Sheepshead minnows (Cyprinodon variegatus), for example, bioconcentrate bis(tributyltin) oxide from seawater up to 2600X in the whole fish (Ward et al. 1981); a 1 $ng.L^{-1}$ (3 $pmol.L^{-1}$ Sn) concentration in the water, for example, will not simply equilibrate with the tissues of many organisms, but will build up to much higher levels with time (see Section 5.5.1.2). Leeuwangh et al. (1976) postulated that at the observed rate of elimination of the triphenyltin moiety from goldfish (Carassius auratus), a lethal triphenyltin residue level would be built up after a few years, even at low external concentrations of triphenyltin compounds. For these and similar reasons, it is essential to consider long-term exposures to low concentrations of organotin compounds.

Other factors to bear in mind when predicting the effects of observed levels of organotin compounds on aquatic organisms include: stage of development, presence of other stresses or pollutants, temperature, salinity, etc. For example, in general the effects of organotin compounds on fry or larvae are greater than those on adult organisms.

Bearing these limitations in mind, one can extract what information is available on the effects of exposures to low concentrations of tributyltin compounds on selected nontarget organisms (Table 7-1) and correlate this information with observed levels. Note that most studies concerned with long-term, low-level exposures have been performed using marine organisms; in contrast, most concentrations of organotin compounds have been measured in Canadian fresh waters. It is apparent from this table that exposures of aquatic organisms to tributyltin concentrations as low as 200 $ng.L^{-1}$ for extended periods of time could lead to serious effects on growth, reproduction and metabolic processes. Since this and higher concentrations of tributyltin compounds have been observed in Canadian fresh waters (primarily in the vicinity of harbors), it is apparent that organotin compounds could have a detrimental effect on fish and other aquatic organisms. More measurements of long-term effects of low levels of tributyltin compounds on Canadian species of aquatic organisms together with measurements of toxicant levels in Canadian fresh waters are needed to confirm this

Table 7-1. The effects of exposures to low concentrations of tributyltin compounds on selected nontarget aquatic organisms.

Compound	Organism^a	Concentration μg.L^{-1}	Concentration nmol.L^{-1} Sn	Exposure time	Comments	Location in text	Reference
Tributyltin chloride	fish	0.4	1.2	6 weeks	effects on enzyme activities		Leeuwangh *et al.* (1976)
"	rainbow trout *Salmo gairdneri* yolk sac fry (fw)	5	15	12 d	lethal	6.4.4, 6.4.5	Seinen *et al.* (1981)
"	"	1	3.1	110 d	diminished glycogen storage; significant decrease in Hb concentration; growth retardation; decrease in body weight	"	"
		0.2	0.62	110 d	diminished glycogen storage; growth retardation; decrease in body weight	"	"
Bis(tributyltin) oxide, tributyltin acetate, chloride	guppy *Lebistes reticulatus* (fw)	21-39	65-130	7 d	50% survival	Table 6-1	Polster and Halacka (1971)
Bis(tributyltin) oxide	sheepshead minnow *Cyprinodon variegatus* (sw)	18	61	7 d	50% survival	Table 6-1	Ward *et al.* (1981)
		1	3.4	14 d	50% survival		
		0.96	3.2	21 d	50% survival		
"	"	0.18-1.0	0.61-3.4	167 d	concluded chronic toxicity not significantly greater than acute toxicity even though bioaccumulation occurred	6.4.5	"
"	North Sea sole *Solea solea* larvae (sw)	2.1	7.1	96 h	50% survival	6.4.1	Thain (1983)
"	teleost *Agonus cataphractus* (sw)	16	54	96 h	50% survival	6.4.1	"
"	4th stage lobster larvae (sw)	1-10	3.4-34		toxic	6.5.1	Jones and Millson (1982)

Table 7-1. (Cont'd)

Compound	Organism^a	Concentration $\mu g.L^{-1}$	Concentration $nmol.L^{-1}$ Sn	Exposure time	Comments	Location in text	Reference
Bis(tributyltin) oxide (cont'd)	lobster Homarus americanus larvae (sw)	20	67	24 h	lethal	6.5.1	Laughlin and French (1980)
		5-15	17-51	up to 6 d	acutely toxic	"	"
		1	3.4		larvae able to metamorphose successfully (same as controls)	"	"
"	sand shrimp Crangon crangon larvae (sw)	1.5	5.1	96 h	50% survival	"	Thain (1983)
"	shore crab Carcinus maenus larvae (sw)	10	34	96 h	50% survival	"	"
"	amphiphod Orchestoidea californiana (sw)	6, 10, and 15	20, 34 and 51	9 d	53, 20 and 7% survival; toxicity apparent only after 5 d of exposure, suggesting short-term toxicity tests may seriously underestimate toxicity	6.5.2.1	Laughlin et al. (1982)
Bis(tributyltin) oxide, tributyltin fluoride	amphipod Gammarus oceanicus adults (sw)	3	10	10-12 d	50% survival	6.5.2.1	Laughlin et al. (1984b)
		3	10	8 weeks	0% survival	"	
	amphipod Gammarus oceanicus larvae (sw)	0.3, 3	1, 10	8 weeks	significant effect on larval survival	"	"
		0.3	1	several weeks	release of larvae reduced or blocked, growth of larvae exposed to bis-(tributyltin) oxide decreased significantly	"	"

Table 7-1. (Cont'd)

Compound	Organism^a	Concentration µg.L^{-1}	Concentration nmol.L^{-1} Sn	Exposure time	Comments	Location in text	Reference
Bis(tributyltin) oxide, tributyltin fluoride (cont'd)	harpacticoid *Nitrocra spinipes* (sw)	1-3	≈3.2-10	96 h	initial concentration killing 50% of organisms	6.5.5	Lindén *et al.* (1979)
Bis(tributyltin) oxide	copepod *Acartia tonsa* (sw)	1 0.75 0.55	3.4 2.5 1.9	96 h 120 h 144 h	50% survival 50% survival 50% survival	6.5.3 " "	U'ren (1983) " "
"	snail *Biomphalaria glabrata* (fw)	10, 1 0.1	34, 3.4 0.34		oviposition inhibited by 100%, >90%, 50%	6.7.2.5	Ritchie *et al.* (1974)
		10	34		newly laid eggs did not develop	"	"
		1	3.4		3% eggs hatched	"	"
		1, 0.1, 0.01, 0.001	3.4, 0.34, 0.034, 0.0034		egg laying of snails exposed continuously to toxicant after hatching significantly reduced in survivors	"	"
		1, 0.1	3.4, 0.34		growth severely retarded	"	"
"	Japanese oyster *Crassostrea gigas* larvae (sw)	1.6	5.4	48 h	50% survival	6.7.3.2	Thain (1983)
"	Japanese oyster *Crassostrea gigas* spat (sw)	0.15	0.51	56 d	decreased growth; pronounced thickening of upper shell valve	6.7.3.2	Waldock and Thain (1983)
		1.6	5.4	56 d	severe inhibition of growth	"	"

Table 7-1. (Cont'd)

Compound	Organism[a]	Concentration µg.L⁻¹	Concentration nmol.L⁻¹ Sn	Exposure time	Comments	Location in text	Reference
Tributyltin acetate	mussel *Mytilus edulis* larvae (sw)	2.3	7.7	48 h	50% survival	6.7.3.2	Thain (1983)
	Japanese oyster *Crassostrea gigas* (sw)	100	290		inhibited fertilization	6.7.3.2	His and Robert (1980)
		10	29		egg cleavage inhibited by 20%	"	"
		5	14		development inhibited	"	"
"	oyster D larvae (sw)	5	14	48 h	100% mortality	"	"
	Japanese oyster *Crassostrea gigas*; mussel *Mytilus galloprovincialis* (sw)	1	2.9		abnormal larvae formed; decreased growth	6.7.3.2	Robert and His (1981)
	Crassostrea gigas (sw)	1	2.9	12 d	100% mortality	"	"
	Mytilus galloprovincialis (sw)	3	8.6	9 d	25% mortality	"	"
Tributyltin species	adult oysters (sw)	0.2	≈0.7	113 d	30% mortality	6.7.3.2	Alzieu *et al.* (1980)
		2	≈7	30 d	100% mortality	"	"
Tributyltin chloride	alga *Euglena gracilis* chloroplasts	6.5	20	15 min	photophosphorylation inhibited	6.9	Kahn (1968)
Bis(tributyltin) oxide	diatom *Skeletonema costatum* (sw)	1-18	3.4-60	5 d	algistatic	6.9	Thain (1983)
"	"	>18	>60	5 d	algicidal	"	"

[a] fw, freshwater; sw, seawater (marine).

speculation. An appropriate conclusion with respect to the effects of butyltin compounds on aquatic organisms in marine and estuarine waters cannot be reached until measurements are made of the levels of butyltin compounds in these waters.

Although there is some information available on the toxic effects of other triorganotin compounds on aquatic organisms (e.g. triethyltin, tripropyltin, triphenyltin), there have been no measurements made of the occurrence of these compounds in Canadian waters, so they will not be discussed further in this section.

A useful tool for viewing the toxicities of triorganotin compounds towards aquatic organisms in perspective would be a comparison of their toxicities with that of another common aquatic pollutant. A good choice for this comparison is copper, because it is one of the few substances, besides triorganotin compounds, that (in the form of copper oxide) is suitable for use as an antifouling agent, i.e. it is lethal in low concentrations for a large number of target organisms, as well as being adequately soluble in seawater. A very rough comparison of the toxic effects of these two pollutants is made in Table 7-2. It should be emphasized that this comparison is extremely crude, taking into account only the quantitative LC_{50} values and virtually ignoring such complicating factors as size of organism, temperature, pH, water hardness, alkalinity, etc. It was felt that a direct comparison of LC_{50} values would be sufficient for our purposes. It can be seen from this table that in all instances, the triorganotin compound is more toxic than copper over a shorter time period. In some cases, the difference in toxicity is as much as 1000-fold. These observations agree with those of Evans and Smith (1975), who made a rough comparison of the antifouling activity of different active substances (Table 7-3), as well as those of His and Robert (1980, 1981b), who compared the effects of copper chloride and tributyltin acetate on the eggs and D larvae of *Crassostrea gigas*.

Table 7-2. A comparison of the toxicities of copper and organotin compounds towards selected aquatic organisms.

Aquatic organism	Copper			Organotin compound		
	Parameter	Concentration	Source	Parameter	Concentration	Source
Lepomis macrochirus (bluegill)	96-h LC_{50}	0.66-2.55 $mg.L^{-1}$ (10-40 $\mu mol.L^{-1}$)	Table 4-1, Spear and Pierce (1979)	48-h TL_m	0.033 $mg.L^{-1}$ triphenyltin hydroxide (0.094 $\mu mol.L^{-1}$ Sn)	Table 6-1
Carassius auratus (goldfish)	96-h LC_{50}	0.036 $mg.L^{-1}$ (0.56 $\mu mol.L^{-1}$)	Table 4-2, Spear and Pierce (1979)	24-h LC_{100}	0.075 $mg.L^{-1}$ bis(tributyltin) oxide (0.25 $\mu mol.L^{-1}$ Sn) 0.4 $mg.L^{-1}$ triphenyltin acetate (1 $\mu mol.L^{-1}$ Sn) 0.25 $mg.L^{-1}$ triphenyltin chloride (0.68 $\mu mol.L^{-1}$ Sn)	Table 6-1
Lebistes reticulatus (guppy)	96-h LC_{50}	0.036-0.31 $mg.L^{-1}$ (0.56-4.8 $\mu mol.L^{-1}$)	Table 4-2, Spear and Pierce (1979)	48-h LC_{50}	0.054 $mg.L^{-1}$ triphenyltin acetate (0.13 $\mu mol.L^{-1}$ Sn)	Table 6-1
				7-d LC_{50}	0.032 $mg.L^{-1}$ triphenyltin acetate (0.078 $\mu mol.L^{-1}$ Sn)	
				7-d LC_{50}	0.039 $mg.L^{-1}$ bis(tributyltin) oxide (0.13 $\mu mol.L^{-1}$ Sn)	
				7-d LC_{50}	0.021 $mg.L^{-1}$ tributyltin chloride (0.065 $\mu mol.L^{-1}$ Sn)	
				7-d LC_{50}	0.028 $mg.L^{-1}$ tributyltin acetate (0.080 $\mu mol.L^{-1}$ Sn)	
Acartia tonsa (calanoid copepod)	96-h LC_{50}	17-55 $\mu g.L^{-1}$ (0.27-0.86 $\mu mol.L^{-1}$)	Sosnowski *et al.* (1979)	96-h LC_{50}	1.0 $\mu g.L^{-1}$ bis(tributyltin) oxide (3.4 $nmol.L^{-1}$ Sn)	Section 6.5.3
				144-h LC_{50}	0.55 $\mu g.L^{-1}$ bis(tributyltin) oxide (1.9 $nmol.L^{-1}$ Sn)	
Nitrocra spinipes (harpacticoid copepod)	24-h LC_{50}	>26 $mg.L^{-1}$ (>406 $\mu mol.L^{-1}$)	Table 4-19, Spear and Pierce (1979)	96-h $LC(I)_{50}$	1-2 $\mu g.L^{-1}$ tributyltin fluoride (3-6 $nmol.L^{-1}$ Sn) 1-3 $\mu g.L^{-1}$ bis(tributyltin) oxide (3-10 $nmol.L^{-1}$ Sn) 6-10 $\mu g.L^{-1}$ triphenyltin fluoride (20-30 $nmol.L^{-1}$ Sn)	Section 6.5.3

Table 7-2. (Cont'd)

Aquatic organism	Copper			Organotin compound		
	Parameter	Concentration	Source	Parameter	Concentration	Source
Daphnia magna (water flea)	48-h LC_{50}	60 $\mu g.L^{-1}$ (0.94 $\mu mol.L^{-1}$)	Table 4-12, Spear and Pierce (1979)	48-h LC_{50}	3.5 $\mu g.L^{-1}$ tributyltin acetate (10 $nmol.L^{-1}$ Sn) 4.8 $\mu g.L^{-1}$ tributyltin chloride (15 $nmol.L^{-1}$ Sn) 2.5 $\mu g.L^{-1}$ bis(tributyltin) oxide (8.4 $nmol.L^{-1}$ Sn)	Section 6.5.4
Biomphalaria glabrata (snail)	24-h LC_{50}	3.2 $mg.L^{-1}$ (50 $\mu mol.L^{-1}$)	Table 4-13, Spear and Pierce (1979)	24-h LC_{50}	0.05-0.1 $mg.L^{-1}$ bis(tripropyltin) oxide (100-200 $nmol.L^{-1}$ Sn) 0.03-0.1 $mg.L^{-1}$ bis(tributyltin) oxide (100-340 $nmol.L^{-1}$ Sn) 0.01-0.05 $mg.L^{-1}$ triphenyltin fluoride (28-140 $nmol.L^{-1}$ Sn)	Table 6-4
Rangia cuneata (clams)	96-h LC_{50}	7.4 $mg.L^{-1}$ (115 $\mu mol.L^{-1}$)	Table 4-18, Spear and Pierce (1979)	5-d LC_{100}	1.0 $mg.L^{-1}$ tributyltin acetate (2.9 $\mu mol.L^{-1}$ Sn)	Section 6.7.3.1
Crassostrea gigas (oyster)	96-h LC_{50}	0.56 $mg.L^{-1}$ (8.8 $\mu mol.L^{-1}$)	Table 4-18, Spear and Pierce (1979)	30-d LC_{100}	2 $\mu g.L^{-1}$ tributyltin species ($\approx$7 $nmol.L^{-1}$ Sn)	Section 6.7.3.2
	14-d LC_{20}	0.1 $mg.L^{-1}$ (1.6 $\mu mol.L^{-1}$)				

Table 7-3. Comparison of the antifouling activities of different active substances (from Evans and Smith 1975).

Active substance	Active concentration ($mg.L^{-1}$)	
	Algae	Barnacles
R_3SnX	0.01-5	0.1-1
R_3PbX	0.1-1	0.1-1
RHgX	0.1-1	0.1-1
Cu_2O	1-50	1-50

APPENDIX I.0 ABBREVIATIONS USED IN TEXT

a	year (annum)
AAS	atomic absorption spectrometry
ASV	anodic stripping voltammetry
ATP	adenosine triphosphate
d	day
DMSO	dimethyl sulfoxide
DNA	deoxyribonucleic acid
Du-Ter	triphenyltin hydroxide
ECD	electron capture detector
EDTA	ethylenediaminetetraacetic acid
FID	flame ionization detector
FPD	flame photometric detector
g	gram
GC	gas chromatography
h	hour
Hb	hemoglobin
HPLC	high-pressure (or high-performance) liquid chromatography
IOTG	isooctyl thioglycolate
LC	liquid chromatography
LC_{50}	concentration of substance killing 50% of test organisms
$LC(I)_{50}$	initial concentration of substance killing 50% of test organisms
LD_{50}	dose required to kill 50% of test organisms
M	molar (moles per litre); or mega ($x10^6$) (prefix)
MDA	minimum detectable amount
MDC	minimum detectable concentration
MIC	minimum inhibitory concentration
MS	mass spectrometry
n	sample size; or number of atoms or molecules, as in R_nSnX_{4-n}; or nano ($x10^{-9}$) (prefix)
NAA	neutron activation analysis
NADP	nicotinamide adenine dinucleotide phosphate
PCV	packed cell volume
Plictran	tricyclohexyltin hydroxide
PVC	poly(vinyl chloride)
QSAR	quantitative structure-activity relationship
RNA	ribonucleic acid
s	second
t	tonne
TLC	thin-layer chromatography
TL_m	mean threshold level
T.N.O.	Toegepast Natuurwetenschappelijk Orderzoek (Dutch Institute for Applied Scientific Research)
TRIT	total recoverable inorganic tin
UV	ultraviolet
Vendex	hexakis (β,β-dimethylphenethyl) stannoxane, hexakis (2-methyl-2-phenylpropyl) distannoxane, di(tri-(2-methyl-2-phenylpropyl)tin) oxide

APPENDIX II.0 GUIDELINES FOR ORGANOTIN COMPOUNDS IN CANADA

There are no environmental standards or regulations for organotin compounds in Canada. However, pest control products (PCP) containing organotin compounds are required to be registered for sale under the federal PCP Act; the Canadian Food and Drug Regulations specify maximum residue levels of organotin compounds for different food products (Table II-1) as well as levels of certain organotin stabilizers to be used in PVC food packaging material; and organotin compounds are listed in proposed regulations under the Transport of Dangerous Goods Act (Jones and Millson 1982).

Table II-1. Maximum residue levels for organotin compounds in Canada (from Jones and Millson 1982)[a].

Compound	Chemical name	Maximum residue ($mg.kg^{-1}$)	Foods
Plictran	tricyclohexyltin hydroxide including the degradation products dicyclohexyltin oxide and monocyclohexylstannoic acid	4.0 2.0 1.0 0.3	Peaches Apples, citrus fruit, dried prunes, pears, strawberries Plums Walnuts
Vendex	di(tri-(2-methyl-2-phenylpropyl)tin) oxide	3.0 2.0 0.5	Apples, pears Citrus fruits Cucumbers, tomatoes

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[a] Some monitoring of Plictran and Du-Ter residues in crop extracts (apples, peaches, potatoes and strawberries) is carried out by the Health Protection Branch of Health and Welfare Canada, using the methods of Breakell *et al*. (1982).

APPENDIX III.0 PROPERTIES OF SELECTED ORGANOTIN COMPOUNDS

Some properties of representative organotin compounds are listed in Tables III-1 to III-4. All compounds known to be in commercial use are included, as are most derivatives listed in the documents "Tin and Organotin Compounds: A Preliminary Review" (WHO 1980), and "Organotins in the Canadian Environment - A Synopsis" (Jones and Millson 1982). The first name given is that used by Chemical Abstracts. This is usually followed by "10CI" indicating that the name was used in the 10th Collective Index. The same name is generally used in 9CI but not necessarily in 8CI. Physical properties are taken primarily from Davies and Smith (1982) and Poller (1970). Occasionally, data from the older review of Ingham *et al*. (1960) are given. The footnotes to all tables are collected together after Table III-4.

Table III-1. Properties of R_4Sn derivatives.

Empirical formula	Compound	Registry No.	Name	mp(°C)	bp[°C(mmHg)]	Notes
$C_4H_{12}Sn$	$(CH_3)_4Sn$	594-27-4	tetramethylstannane (10CI)	-54	77(760)	
$C_8H_{20}Sn$	$(C_2H_5)_4Sn$	597-04-8	tetraethylstannane (10CI)	-136 to -126	181 63-65(12)	
$C_{12}H_{28}Sn$	$(C_3H_7)_4Sn$	2176-98-9	tetrapropylstannane (10CI)		131(760)	
$C_{16}H_{36}Sn$	$(C_4H_9)_4Sn$	1461-25-2	tetrabutylstannane (10CI)		127(1.7) 145(10)	
$C_{24}H_{20}Sn$	$(C_6H_5)_4Sn$	545-90-4	tetraphenylstannane (10CI)	225		
$C_{24}H_{44}Sn$	$(C_6H_{11})_4Sn$	1449-55-4	tetracyclohexylstannane (10CI)	261-263		
$C_{32}H_{68}Sn$	$(C_8H_{17})_4Sn$	3540-84-9	tetraoctylstannane (10CI)		268(10)	
$C_{48}H_{100}Sn$	$(C_{12}H_{25})_4Sn$	5827-56-5	tetradodecylstannane (10CI)			
$C_{72}H_{148}Sn$	$(C_{18}H_{37})_4Sn$	23285-56-5	tetraoctadecylstannane (8CI)		250-270(760)	
$C_7H_{18}Sn$	$(CH_3)_3SnC_4H_9$	1527-89-7	butyltrimethylstannane (10CI)		149-150(724)	
$C_{10}H_{24}Sn$	$(CH_3)_2Sn(C_4H_9)_2$	1528-00-3	dibutyldimethylstannane (10CI)		70(4.4)	
$C_{13}H_{30}Sn$	$CH_3Sn(C_4H_9)_3$	1528-01-4	tributylmethylstannane (10CI)		122-124(12)	
$C_{40}H_{52}Sn$	$(C_6H_5C(CH_3)_2CH_2)_4Sn$	1262-78-8	tetrakis (2-methyl-2-phenylpropyl) stannane (9CI)			

Table III-2. Properties of R_3SnX derivatives.

Empirical formula	Compound	Registry No.	Name	mp(°C)	bp[°C(mmHg)]	Notes
Halogen-bound Derivatives						
C_3H_9FSn	$(CH_3)_3SnF$	420-60-0	fluorotrimethylstannane (10CI); trimethyltin fluoride	375(d)		
C_3H_9ClSn	$(CH_3)_3SnCl$	1066-45-1	chlorotrimethylstannane (10CI); trimethyltin chloride	37-38		
C_3H_9BrSn	$(CH_3)_3SnBr$	1066-44-0	bromotrimethylstannane (10CI); trimethyltin bromide	26-27		
C_3H_9ISn	$(CH_3)_3SnI$	811-73-4	iodotrimethylstannane (10CI); trimethyltin iodide		67-68(15)	
$C_6H_{15}ClSn$	$(C_2H_5)_3SnCl$	994-31-0	chlorotriethylstannane (10CI); triethyltin chloride		210(760)	
$C_6H_{15}BrSn$	$(C_2H_5)_3SnBr$	2767-54-6	bromotriethylstannane (10CI); triethyltin bromide		224(760)	
$C_6H_{15}ISn$	$(C_2H_5)_3SnI$	2943-86-4	triethyliodostannane (10CI); triethyltin iodide		234(760)	
$C_9H_{21}ClSn$	$(C_3H_7)_3SnCl$	2279-76-7	chlorotripropylstannane (10CI); tripropyltin chloride		98-100(4)	
$C_{12}H_{27}ClSn$	$(C_4H_9)_3SnCl$	1461-22-9	tributylchlorostannane (10CI); tributyltin chloride		152-156(14)	
$C_{12}H_{27}FSn$	$(C_4H_9)_3SnF$	1983-10-4	tributylfluorostannane (10CI); tributyltin fluoride	248-252		a
$C_{18}H_{15}ClSn$	$(C_6H_5)_3SnCl$	639-58-7	chlorotriphenylstannane (10CI); triphenyltin chloride; LS 4442; GC 8993; General Chemicals 8993; TPTC; HUE 2872; Brestanol; Fentin chloride	105		a
$C_{18}H_{15}FSn$	$(C_6H_5)_3SnF$	379-52-2	fluorotriphenylstannane (10CI); triphenyltin fluoride	357(d)		
$C_{18}H_{33}ClSn$	$(C_6H_{11})_3SnCl$	3091-32-5	chlorotricyclohexylstannane (10CI); tricyclohexyltin chloride	129-130		

Table III-2. (Cont'd)

Empirical formula	Compound	Registry No.	Name	mp(°C)	bp[°C(mmHg)]	Notes
Halogen-bound Derivatives (Cont'd)						
$C_{24}H_{51}ClSn$	$(C_8H_{17})_3SnCl$	2587-76-0	chlorotrioctylstannane (10CI); trioctyltin chloride		163-166(10^{-2})	
Oxygen-bound Derivatives						
$C_3H_{10}OSn$	$(CH_3)_3SnOH$	56-24-6	hydroxytrimethylstannane (10CI); trimethyltin hydroxide	117-118		
$C_6H_{18}OSn_2$	$[(CH_3)_3Sn]_2O$	1692-18-8	hexamethyldistannoxane (10CI); bis(trimethyltin) oxide		86(24)	
$C_6H_{16}OSn$	$(C_2H_5)_3SnOH$	994-32-1	triethylhydroxystannane (10CI); triethyltin hydroxide	48-50		
$C_{12}H_{30}OSn_2$	$[(C_2H_5)_3Sn]_2O$	1112-63-6	hexaethyldistannoxane (10CI); bis(triethyltin) oxide		76-79(10^{-1})	
$C_{12}H_{28}OSn$	$(C_4H_9)_3SnOH$	1067-97-6	tributylhydroxystannane (10CI); tributyltin hydroxide	15-16		
$C_{24}H_{54}OSn_2$	$[(C_4H_9)_3Sn]_2O$	56-35-9	hexabutyldistannoxane (10CI); bis(tributyltin) oxide; tributyltin oxide; C-Sn-9; BioMet TBTO; Butinox; TBTO; Lastanox T; Vikov AF-25; Vikol LO-25; BioMet 66; BioMet SRM; Lastanox Q; Lastanox F; Stannicide A; Mykolastanox F		154-158(0.25) 25 ($1.6x10^{-3}$) (est.)	a,b,c, d
$C_{18}H_{16}OSn$	$(C_6H_5)_3SnOH$	76-87-9	hydroxytriphenylstannane (10CI); triphenyltin hydroxide; K 19 (VAN); Tenhide; Fenolovo; Du-Ter Extra; Erithane; Vancide K.S.; Dowco 186; ENT 29004; Du-Ter; Fentin hydroxide	116-120		a,e
$C_{36}H_{30}OSn_2$	$[(C_6H_5)_3Sn]_2O$	1262-21-1	hexaphenyldistannoxane (10CI); bis(triphenyltin) oxide	117.5-118		
$C_{60}H_{78}OSn_2$	$[(C_6H_5C(CH_3)_2CH_2)_3Sn]_2O$		hexakis(2-methyl-2-phenylpropyl)distannoxane (10CI); bis(tris(2-methyl-2-phenyl)tin) oxide; Fenbutatin oxide; Vendex; Torque	138-139		f

Table III-2. (Cont'd)

Empirical formula	Compound	Registry No.	Name	mp(°C)	bp[°C(mmHg)]	Notes
Oxygen-bound Derivatives (Cont'd)						
$C_{18}H_{34}OSn$	$(C_6H_{11})_3SnOH$	13121-70-5	tricyclohexylhydroxystannane (10CI); tricyclohexyltin hydroxide; Plictran; Plyctran; M 3180; cyhexatin; Dow Co 213; ENT-27395	195-198		f
$C_{36}H_{66}OSn_2$	$[(C_6H_{11})_3Sn]_2O$	5837-26-3	hexacyclohexyldistannoxane (10CI); bis(tricyclohexyltin) oxide			
$C_{19}H_{32}O_2Sn$	$(C_4H_9)_3SnO(O)CC_6H_5$	4342-36-3	(benzoyloxy)tributylstannane (10CI); tributyltin benzoate			g
$C_{16}H_{32}O_2Sn$	$(C_4H_9)_3SnO(O)CCH{=}CHCH_3$	2155-70-6	[tributyl(2-methyl-1-oxo-2-propenyl)-oxy]stannane (10CI); tributyltin methacrylate			
$C_{24}H_{50}O_2Sn$	$(C_4H_9)_3SnO(O)CC_{11}H_{23}$	3090-36-6	tributyl[(1-oxododecyl)oxy]stannane (10CI); tributyltin laurate	14-15	180-185(2)	
$C_{30}H_{60}O_2Sn$	$(C_4H_9)_3SnO(O)CC_{17}H_{33}$	3090-35-5	tributyl[(1-oxo-9-octadecenyl)oxy]-stannane (Z) (10CI); tributyltin oleate; N 5117 (Stauffer); N5117			
$C_{20}H_{42}O_2Sn$	$(C_6H_{13})_3SnO(O)CCH_3$	2897-46-3	(acetyloxy)trihexylstannane (9CI); trihexyltin acetate			
$C_{20}H_{18}O_2Sn$	$(C_6H_5)_3SnO(O)CCH_3$	900-95-8	(acetyloxy)triphenylstannane (10CI); triphenyltin acetate; Brestan; Batasan; Phentin acetate; Suzu; GC 6936; ENT 25208; Fentin acetate; Lirostanol; TPTA; VP 19-40; Brestan 60; Liromatin; Fennite	122-124		a,e
$C_{12}H_{30}O_4SSn_2$	$[(C_2H_5)_3Sn]_2SO_4$	57-52-3	3,3,7,7-tetraethyl-4,6-dioxa-5-thia-3,7-distannanonane; 5,5-dioxide (10CI); triethyltin sulfate			
$C_8H_{18}O_2Sn$	$(C_2H_5)_3SnO(O)CCH_3$	1907-13-7	(acetyloxy)triethylstannane (10CI); triethyltin acetate			
$C_{12}H_{21}Cl_3O_2Sn$	$(C_2H_5)_3SnOCH(OC_4H_5)CCl_3$	17869-91-9	[1-(3-butynyloxy)-2,2,2-trichloro-ethoxy]triethylstannane (8CI)			

Table III-2. (Cont'd)

Empirical formula	Compound	Registry No.	Name	mp(°C)	bp[°C(mmHg)]	Notes
Oxygen-bound Derivatives (Cont'd)						
$C_{14}H_{30}O_2Sn$	$(C_4H_9)_3SnO(O)CCH_3$	56-36-0	(acetyloxy)tributylstannane (10CI); tributyltin acetate	121-122 (80-83)		a
$C_{30}H_{58}O_2Sn$	$(C_4H_9)_3SnO(O)CC_{17}H_{31}$	24124-25-2	tributyl[(1-oxo-9,12-octadecadienyl)-oxy]stannane (Z,Z) (10CI); tributyltin linoleate			
$(C_{16}H_{32}O_2Sn)_n$	$(-CHCH_3CHCOOSn(C_4H_9)_3)_n$	26354-15-4	tributyl[(2-methyl-1-oxo-2-propenyl)oxy]-stannane [2155-70-6] homopolymer (10CI)			a,h
	$(C_4H_9)_3SnO(O)O(Naphth)$		tributyltin naphthenate			b,i,x
$C_{30}H_{62}O_4Sn_2$	$(C_4H_9)_3SnO(O)CCH_2CH_2-)_2$	7437-35-6	5,5,14,14-tetrabutyl-7,12-dioxo-6,13-dioxa-5,14-distannaoctadecane (10CI)			a
$C_{36}H_{81}O_4PSn_3$	$[(C_4H_9)_3Sn]_3PO_4$	13435-05-7	5,5,9,9-tetrabutyl-7-[(tributylstannyl)-oxy]-6,8-dioxa-7-phospha-6,9-distannatridecane (10CI); tributyltin phosphate			b
Sulfur-bound Derivatives						
$C_{24}H_{54}SSn_2$	$[(C_4H_9)_3Sn]_2S$	4808-30-4	hexabutyl distannathiane (10CI); tributyltin sulfide; Nofoul			
Hydrogen-bound Derivatives						
$C_3H_{10}Sn$	$(CH_3)_3SnH$	1631-73-8	trimethylstannane (10CI); trimethyltin hydride		59(740)	
$C_6H_{16}Sn$	$(C_2H_5)_3SnH$	997-50-2	triethylstannane (10CI); triethyltin hydride		148-150(760)	
$C_{12}H_{28}Sn$	$(C_4H_9)_3SnH$	688-73-3	tributylstannane (10CI); tributyltin hydride		76-81(0.7)	
$C_{18}H_{16}Sn$	$(C_6H_5)_3SnH$	892-20-6	triphenylstannane (10CI); triphenyltin hydride	28	168-170(0.5)	
$C_{18}H_{34}Sn$	$(C_6H_{11})_3SnH$	6056-50-4	tricyclohexylstannane (10CI); tricyclohexyltin hydride			

Table III-2. (Cont'd)

Empirical formula	Compound	Registry No.	Name	mp(°C)	bp[°C(mmHg)]	Notes
Hydrogen-bound Derivatives (cont'd)						
$C_{24}H_{52}Sn$	$(C_8H_{17})_3SnH$	869-59-0	trioctylstannane (10CI); trioctyltin hydride		$143(10^{-3})$	
Nitrogen-bound Derivatives						
$C_{20}H_{17}N_3Sn$	$(C_6H_5)_3SnC_2H_2N_3$	974-29-8	1-(triphenylstannyl)-1H-1,2,4-triazole (9CI); triphenyltin triazole			
$C_{20}H_{35}N_3Sn$	$(C_6H_{11})_3SnC_2H_2N_3$	41083-11-8	1-(tricyclohexylstannyl)-1H-1,2,4-triazole (10CI); tricyclohexyltin triazole; Azocyclotin; Peropal	218.8		f

Table III-3. Properties of R_2SnX_2 derivatives.

Empirical formula	Compound	Registry No.	Name	mp(°C)	bp[°C(mmHg)]	Notes
Halogen-bound Derivatives						
$C_2H_6Cl_2Sn$	$(CH_3)_2SnCl_2$	753-73-1	dichlorodimethylstannane (10CI); dimethyltin dichloride	107-108		j
$C_4H_{10}Cl_2Sn$	$(C_2H_5)_2SnCl_2$	866-[illegible]	dichlorodiethylstannane (10CI); diethyltin dichloride	84		
$C_4H_{10}I_2Sn$	$(C_2H_5)_2SnI_2$	2767-55-7	diethyldiiodostannane (10CI); diethyltin diiodide	44		
$C_6H_{14}Cl_2Sn$	$(C_3H_7)_2SnCl_2$	807-36-7	dichlorodipropylstannane (10CI); dipropyltin dichloride	81		
$C_8H_{18}Cl_2Sn$	$(C_4H_9)_2SnCl_2$	683-18-1	dibutyldichlorostannane (10CI); dibutyltin dichloride	40-41	135(10)	
$C_{10}H_{22}Cl_2Sn$	$(C_5H_{11})_2SnCl_2$	1118-42-9	dichlorodipentylstannane (10CI); dipentyltin dichloride			
$C_{12}H_{10}Cl_2Sn$	$(C_6H_5)_2SnCl_2$	1135-99-5	dichlorodiphenylstannane (10CI); diphenyltin dichloride	41-42		
$C_{12}H_{22}Cl_2Sn$	$(C_6H_{11})_2SnCl_2$	3342-69-6	dichlorodicyclohexylstannane (10CI); dicyclohexyltin dichloride	88-89		
$C_{16}H_{34}Cl_2Sn$	$(C_8H_{17})_2SnCl_2$	3542-36-7	dichlorodioctylstannane (10CI); dioctyltin dichloride	47		
$C_{24}H_{50}Cl_2Sn$	$(C_{12}H_{25})_2SnCl_2$	5827-58-7	dichlorodidodecylstannane (9CI); didodecyltin dichloride			
$C_{24}H_{50}Br_2Sn$	$(C_{12}H_{25})_2SnBr_2$	65264-08-6	dibromodidodecylstannane (10CI); didodecyltin dibromide			

Table III-3. (Cont'd)

Empirical formula	Compound	Registry No.	Name	mp(°C)	bp[°C(mmHg)]	Notes
Halogen-bound Derivatives (Cont'd)						
$C_{36}H_{74}Cl_2Sn$	$(C_{18}H_{37})_2SnCl_2$	-	dichlorodioctadecylstannane; dioctadecyltin dichloride			
$C_{36}H_{74}Br_2Sn$	$(C_{18}H_{37})_2SnBr_2$	65264-09-7	dibromodioctadecylstannane (10CI); dioctadecyltin dibromide			
Oxygen-bound Derivatives						
C_2H_6OSn	$(CH_3)_2SnO$	2273-45-2	dimethyloxostannane (10CI); dimethyltin oxide			
$C_4H_{10}OSn$	$(C_2H_5)_2SnO$	3682-12-0	diethyloxostannane (10CI); diethyltin oxide			
$C_8H_{18}OSn$	$(C_4H_9)_2SnO$	818-08-6	dibutyloxostannane (10CI); dibutyltin oxide	110-115		
$C_{12}H_{10}OSn$	$(C_6H_5)_2SnO$	2273-51-0	oxodiphenylstannane (10CI); diphenyltin oxide	38		
$C_{12}H_{22}OSn$	$(C_6H_{11})_2SnO$	22771-17-1	dicyclohexyloxostannane (10CI); dicyclohexyltin oxide			
$C_{16}H_{34}OSn$	$(C_8H_{17})_2SnO$	870-08-6	dioctyloxostannane (10CI); dioctyltin oxide			
$C_{24}H_{40}O_8Sn$	$(C_4H_9)_2Sn(O(O)CCH{=}CHC(O)OC_4H_9)_2$	15546-16-4	6,6-dibutyl-4,8,11-trioxo-5,7,12-trioxa-6-stannahexadeca-2,9-dienoic acid, butyl ester (Z,Z) (10CI); dibutyltin di(butyl maleate); maleic acid dibutyltin salt (2:1); B5[stabilizer]			k

Table III-3. (Cont'd)

Empirical formula	Compound	Registry No.	Name	mp(°C)	bp[°C(mmHg)]	Notes
Oxygen-bound Derivatives (Cont'd)						
$C_{34}H_{60}O_8Sn$	$(C_4H_9)_2Sn(O(O)CCH=CHC(O)OC_9H_{19})_2$	10584-97-1	dibutylbis[(3-carboxyacryloyl)oxy)-stannane dinonyl ester (8CI); dibutyltin di(nonyl maleate)			
	"$(C_4H_9)_2Sn(OOCC_{11}H_{23})-(OOCCH=CHCOOH)_2$"	73246-84-1	dibutyltin "laurate-maleate"; 1:1 mixture of 77-58-7 and dibutyltin dimaleate; Thermolite 17; Thermolite			
$C_{12}H_{24}O_4Sn$	$(C_4H_9)_2Sn(OOCCH_3)_2$	1067-33-0	bis(acetyloxy)dibutylstannane (10CI); dibutyltin acetate; T 1[catalyst]; T 1(VAN); Ba 2726	8.5-10	142-145(10)	l
$C_{32}H_{64}O_4Sn$	$(C_4H_9)_2Sn(OOCC_{11}H_{23})_2$	77-58-7	dibutylbis[(1-oxododecyl)oxy]stannane (10CI); dibutyltin laurate; Butynorate; DBTL; Stabilizer D-22; Stanclere DBTL; Davainex; TVS Tin Lau; Mark 1038; Tinostat; Stavinor 1200 SN; T 12 (catalyst); T 12 (VAN); Mark 1038; Advastab DBTL; Niax D-22; Clear 1; Wormal CC-1; Ferro 820	22-24	205(10)	k,l, m,n
$C_{12}H_{20}O_4Sn$	$(C_4H_9)_2\overline{SnO(O)CCH=CHC(O)O}$	78-04-6	2,2-dibutyl-1,3,2-dioxastannepin-7,4-dione (10CI); dibutyltin maleate; Advastab DBTM; Advastab T 290; Stavinor 1300 SN: Advastab T 340; Nuodex V 1525; Irgastab T 290	69-70 (mono hydrate) 110		k
$C_{24}H_{48}O_4Sn$	$(C_4H_9)_2Sn(OOCC_7H_{15})_2$	4731-77-5	dibutylbis[(1-oxooctyl)oxy]stannane (10CI); dibutyltin dioctanoate			
$C_{20}H_{40}O_4Sn$	$(C_8H_{17})_2Sn(O(O)CCH_3)_2$	17586-94-6	bis(acetyloxy)dioctylstannane (10CI); dioctyltin acetate			

Table III-3. (Cont'd)

Empirical formula	Compound	Registry No.	Name	mp(°C)	bp[°C(mmHg)]	Notes
Oxygen-bound Derivatives (Cont'd)						
$C_{40}H_{80}O_4Sn$	$(C_8H_{17})_2Sn(O(O)CC_{11}H_{23})_2$	3648-18-8	dioctylbis[(1-oxododecyl)oxy]stannane (10CI); dioctyltin dilaurate			
$C_{20}H_{36}O_4Sn$	$(C_8H_{17})_2\overline{SnO(O)CCH=CHC(O)O}$	16091-18-2	2,2-dioctyl-1,3,2-dioxastannepin-4,7-dione (10CI); dioctyltin maleate; Thermolite 813; Estabex U 18; Mellite 825			k,o
$C_{32}H_{56}O_8Sn$	$(C_8H_{17})_2Sn(O(O)CCH=CHC(O)OC_4H_9)_2$	29575-02-8	6,6-dioctyl-4,8,11-trioxo-5,7,12-trioxa-6-stannahexadeca-2,9-dienoic acid, butyl ester (Z,Z) (10CI); dioctyltin di(butyl maleate)			
$C_{32}H_{56}O_8Sn$	$(C_8H_{17})_2Sn(O(O)CCH=CHC(O)OC_4H_9\text{-}i)_2$	15571-59-2	bis[(3-carboxyacryloyl)oxy]dioctylstannane diisobutyl ester (8CI); dioctyltin bis-(isobutyl maleate)			
$C_6H_8O_4Sn$	$(CH_3)_2\overline{SnO(O)CCH=CHC(O)O}$	22535-43-9	2,2-dimethyl-1,3,2-dioxastannepin-4,7-dione (9CI); dimethyltin maleate			k
$C_{16}H_{24}O_8Sn$	$(C_4H_9)_2Sn(O(O)CCH=CHCOOH)_2$	10192-92-4	4,4'-[(dibutylstannylene)bis(oxy)]bis-(4-oxo-2-butenoic acid) (Z,Z) (10CI); dibutyltin dimaleate			
$C_{24}H_{40}O_8Sn$	$(C_8H_{17})_2Sn(O(O)CCH=CHCOOH)_2$	15571-60-5	4,4'-[(dioctylstannylene)bis(oxy)] bis-(4-oxo-2-butenoic acid) (Z,Z) (10CI); dioctyltin dimaleate			
$C_{18}H_{28}O_8Sn$	$(C_4H_9)_2Sn(O(O)CCH=CHC(O)OCH_3)_2$	15546-11-9	6,6-dibutyl-4,8,11-trioxo-5,7,12-trioxa-6-stannatrideca-2,9-dienoic acid, methyl ester (Z,Z) (10CI); dibutyltin di(methyl maleate)			k,r

Table III-3. (Cont'd)

Empirical formula	Compound	Registry No.	Name	mp(°C)	bp[°C(mmHg)]	Notes
Oxygen-bound Derivatives (Cont'd)						
$C_{32}H_{56}O_8Sn$	$(C_4H_9)_2Sn(O(O)CCH{=}CHC(O)OC_8H_{17})_2$	25168-21-2	4,4'-[(dibutylstannylene) bis(oxy)]bis-[4-oxo-2-butenoic acid] diisooctyl ester (Z,Z) (10CI); dibutyltin di-(isooctyl maleate); dibutyltin bis-(isooctyl maleate); Thermolite 26; Advastab T-150; Mark 275	43	153(10)	k,r
$C_{34}H_{64}O_8S_2Sn$	$(C_4H_9O(O)CCH_2CH_2)_2Sn(SCH_2C(O)OC_8H_{17}\text{-}i)_2$	63397-60-4	3,3'-[bis(2-(isooctyl)-2-oxoethyl)thio]-stannylene-bispropanoic acid, dibutyl ester (10CI); bis(β-carbobutoxy)tin bis(isooctyl thioglycollate)			k
Sulfur-bound Derivatives						
$C_8H_{18}SSn$	$(C_4H_9)_2SnS$	4253-22-9	dibutylthioxostannane (10CI); dibutyltin sulfide			k
$C_{22}H_{44}O_4S_2Sn$	$(CH_3)_2Sn(SCH_2COOC_8H_{17})_2$	26636-01-1	2,2'-[(dimethylstannylene)bis(thio)]-bisacetic acid diisooctyl ester (10CI); dimethyltin bis(isooctyl thioglycollate); dimethyltin S,S-bis(isooctyl mercaptoacetate); TM 181; T 40 (ester); TM 181S; Advastab TM 181S; TM 181FS; TM-387; Thermolite 106; Mark 1900; 1920A			
$C_{11}H_{22}O_2SSn$	$(C_4H_9)_2\overline{Sn\text{-}SCH_2CH_2C(O)O}$	78-06-8	2,2-dibutyldihydro-6H-1,3,2,-oxathiastannin-6-one (10CI); dibutyltin β-mercaptopropanoate; dibutyltin O,S'-mercaptopropionate; Thermolite 35; Advastab T-306; Mark 488			
$C_{26}H_{56}S_2Sn$	$(CH_3)_2Sn(SC_{12}H_{25})_2$	51287-84-4	bis(dodecyithia)dimethylstannane (10CI); dimethyltin bis(laurylmercaptide)			k,q

Table III-3. (Cont'd)

Empirical formula	Compound	Registry No.	Name	mp(°C)	bp[°C(mmHg)]	Notes
Sulfur-bound Derivatives (Cont'd)						
$C_{32}H_{68}S_2Sn$	$(C_4H_9)_2Sn(SC_{12}H_{25})_2$	1185-81-5	dibutylbis(dodecylthio)stannane (10CI); dibutyltin bis(laurylmercaptide); dibutyltin bis(dodecylmercaptide); Mellite 39; Advastab TM98; Mellite 139; Thermolite 20; Ferro 822; Mark A; CC-10			c,k, l,m
$C_{28}H_{56}O_4S_2Sn$	$(C_4H_9)_2Sn(SCH_2COOC_8H_{17}\text{-}i)_2$	25168-24-5	2,2'-(dibutylstannylene)bis(thio)bisacetic acid, diisooctyl ester (10CI); dibutyltin bis(isooctyl thioglycollate); dibutyltin S,S'-bis(isooctyl mercaptoacetate); Thermolite 31; BTS 70; T 101 (accelerator); Irgastab 17M; T 101			k,p
$C_{36}H_{72}O_4S_2Sn$	$(C_8H_{17})_2Sn(SCH_2COOC_8H_{17})_2$	15571-58-1	10-ethyl-4,4-dioctyl-7-oxo-8-oxa-3,5-dithia-4-stannatetradecanoic acid, 2-ethylhexyl ester (10CI); dioctyltin bis(2-ethylhexyl mercaptoacetate); dioctyltin bis(2-ethylhexyl thioglycollate); Advastab 17 MOK			k
$C_{44}H_{88}O_4S_2Sn$	$(C_8H_{17})_2Sn(SCH_2COOC_{12}H_{25})_2$	73246-85-2	4,4-dioctyl-7-oxa-8-oxa-3,5-dithia-4-stanneicosanoic acid, dodecyl ester (10CI); dioctyltin bis(lauryl mercaptoacetate); dioctyltin bis(lauryl thioglycollate)			
$C_{40}H_{84}S_2Sn$	$(C_8H_{17})_2Sn(SC_{12}H_{25})_2$	22205-30-7	bis(dodecylthio)dioctylstannane (10CI); dioctyltin bis(lauryl mercaptide)			
$C_{24}H_{46}O_4S_2Sn$	$(C_8H_{17})_2\overline{Sn\text{-}SCH_2C(O)O(CH_2)_4C(O)OCH_2S}$		5,5-dioctyl-1,9-dioxa-4,6-dithia-5-stannacyclotridecane-2,8-dione (10CI); dioctyltin S,S-(1,4-butanediolbis-mercaptoacetate)			

Table III-3. (Cont'd)

Empirical formula	Compound	Registry No.	Name	mp(°C)	bp[°C(mmHg)]	Notes
Sulfur-bound Derivatives (Cont'd)						
$C_{36}H_{72}O_4S_2Sn$	$(C_8H_{17})_2Sn(SCH_2COOC_8H_{17}\text{-}i)_2$	26401-97-8	2,2'-(dioctylstannylene)bis(thio)-bisacetic acid diisooctyl ester (10CI); dioctyltin S,S'-bis(isooctyl mercaptoacetate); dioctyltin bis(isooctyl thioglycollate; Mellite 831C; Irgastab 17 MOK; Octyl 11; Mark OTM; Thermolite 831			k
$C_{18}H_{36}O_2SSn$	$(C_8H_{17})_2\overline{Sn\text{-}S\text{-}CH_2C(O)O}$	15535-79-2	2,2-dioctyl-1,3,2-oxothiastannolan-5-one (10CI); dioctyltin mercaptoacetate			
$C_{19}H_{38}O_2SSn$	$(C_8H_{17})_2Sn\text{-}S\text{-}CH_2CH_2C(O)O$	3033-29-2	dioctyl-dihydro-2,2-6H-1,3,2-oxathiastannin-6-one (10CI); dioctyltin mercaptopropionate; Advastab T-270; Mark 492			
$C_{28}H_{56}O_4S_2Sn$	$(C_8H_{17})_2Sn(SCH_2COOC_4H_9)_2$	27107-88-6	4,4-dioctyl-7-oxo-8-oxa-3,5-dithia-4-stannadodecanoic acid butyl ester (10CI); dioctyltin bis(butyl mercaptoacetate); dioctyltin bis(butyl thioglycollate)			
Hydrogen-bound Derivatives						
C_2H_8Sn	$(CH_3)_2SnH_2$	2067-76-7	dimethylstannane (10CI); dimethyltin hydride		35(760)	
$C_4H_{12}Sn$	$(C_2H_5)_2SnH_2$	871-33-0	diethylstannane (10CI); diethyltin hydride		80(760)	
$C_8H_{20}Sn$	$(C_4H_9)_2SnH_2$	1002-53-5	dibutylstannane (10CI); dibutyltin hydride		70(12)	
$C_{12}H_{12}Sn$	$(C_6H_5)_2SnH_2$	1011-95-6	diphenylstannane (10CI); diphenyltin hydride		89-93(0.3)	
$C_{12}H_{24}Sn$	$(C_6H_{11})_2SnH_2$	7529-52-4	dicyclohexylstannane (9CI); dicyclohexyltin hydride			
$C_{16}H_{36}Sn$	$(C_8H_{17})_2SnH_2$	15231-44-4	dioctylstannane (10CI); dioctyltin hydride			

Table III-4. Properties of $RSnX_3$ derivatives.

Empirical formula	Compound	Registry No.	Name	mp(°C)	bp[°C(mmHg)]	Notes
CH_3Cl_3Sn	CH_3SnCl_3	993-16-8	trichloromethylstannane (10CI); methyltin trichloride	45-46	176(760)	j
$C_2H_5Cl_3Sn$	$C_2H_5SnCl_3$	1066-57-5	trichloroethylstannane (10CI); ethyltin trichloride	-10	86(12) 94(13)	
$C_2H_5I_3Sn$	$C_2H_5SnI_3$	3646-94-46	ethyltriiodostannane (10CI); ethyltin triiodide		181-184.5(19)	
$C_3H_7Cl_3Sn$	$C_3H_7SnCl_3$	2767-56-8	trichloropropylstannane (10CI); propyltin trichloride		98-99(12)	
$C_4H_9Cl_3Sn$	$C_4H_9SnCl_3$	1118-46-3	butyltrichlorostannane (10CI); butyltin trichloride		93(10)	
$C_4H_7Cl_3O_2Sn$	$CH_3OOC(CH_2)_2SnCl_3$	72883-58-0	trichloro(3-methoxy-3-oxopropyl)tin (10CI)	69-70	174(4)	
$C_6H_5Cl_3Sn$	$C_6H_5SnCl_3$	1124-19-2	trichlorophenylstannane (10CI); phenyltin trichloride	-31	90(0.7)	
$C_6H_{11}Cl_3Sn$	$C_6H_{11}SnCl_3$	3091-31-4	trichlorocyclohexylstannane (9CI); cyclohexyltin trichloride			
$C_7H_{13}Cl_3O_2Sn$	$C_4H_9OOC(CH_2)_2SnCl_3$	61470-34-6	3-(trichlorostannyl)propanoic acid butyl ester (10CI)	46		
$C_8H_{17}Cl_3Sn$	$C_8H_{17}SnCl_3$	3091-25-6	trichlorooctylstannane (10CI); octyltin trichloride		115(0.2)	
$C_{12}H_{25}Cl_3Sn$	$C_{12}H_{25}SnCl_3$	51375-45-2	trichlorododecylstannane (10CI); dodecyltin trichloride		93-95(5x10^{-4})	
$C_{18}H_{37}Cl_3Sn$	$C_{18}H_{37}SnCl_3$	54254-09-0	trichlorooctadecylstannane (9CI); octadecyltin trichloride		≈100(5x10^{-4})	
Oxygen-bound Derivatives						
CH_4O_2Sn	$CH_3SnO(OH)$	753-61-7	hydroxymethyloxostannane (10CI); methylstannonic acid			
$C_4H_{10}O_2Sn$	$C_4H_9SnO(OH)$	2273-43-0	butylhydroxyoxostannane (10CI); butylstannonic acid (VAN)			

Table III-4. (Cont'd)

Empirical formula	Compound	Registry No.	Name	mp(°C)	bp[°C(mmHg)]	Notes
Oxygen-bound Derivatives (Cont'd)						
$C_4H_{10}OSSn$	$C_4H_9SnO(SH)$	26410-42-4	butylmercaptooxostannane (10CI): butylthiostannonic acid			
$C_6H_{12}O_2Sn$	$C_6H_{11}SnO(OH)$	22771-18-2	cyclohexylhydroxyoxostannane (9CI); cyclohexylstannonic acid			
$C_8H_{18}O_2Sn$	$C_8H_{17}SnO(OH)$	13356-20-2	hydroxyoctyloxostannane (10CI); octylstannoic acid			
$C_{10}H_{21}NO_3Sn$	$C_4H_9Sn(OCH_2CH_2)_3N$	50688-91-0	butyl[[2,2',2"-nitrilotris[ethanolato]]-(3-)-N,O,O'O"]tin (10CI)	158.9		s
$C_{12}H_{17}NO_3Sn$	$C_6H_5Sn(OCH_2CH_2)_3N$	55610-14-5	[[2,2',2"-nitrilotris[ethanolato]](3-)-N,O,O',O"]phenyltin	220(d)		t
$C_{14}H_{29}NO_3Sn$	$C_8H_{17}Sn(OCH_2CH_2)_3N$	38979-15-6	[[2,2',2"-nitrilotris[ethanolato]](3-)-N,O,O',O"]octyltin	112-122		s
Sulfur-bound Derivatives						
$C_8H_{18}S_3Sn_2$	$(C_4H_9SnS_{3/2})_2$	15666-29-2	dibutyldithioxodistannathiane (10CI); butyltin sulfide	230(d)		k
$C_{31}H_{60}O_6S_3Sn$	$CH_3Sn(SCH_2COOC_8H_{17}\text{-}i)_3$	54849-38-6	2,2',2"-[(methylstannylidyne)tris(thio)]-trisacetic acid, triisooctyl ester (10CI); methyltin tris(isooctyl thioglycolate)			k,u
$C_{34}H_{66}O_6S_3Sn$	$C_4H_9Sn(SCH_2COOC_8H_{17}\text{-}i)_3$	25852-70-4	2,2',2"-[(butylstannylidyne)tris(thio)]-trisacetic acid, triisooctyl ester (10CI); butyltin tris(isooctyl thioglycolate)			k,p,u
$C_{37}H_{70}O_8S_3Sn$	$C_4H_9OOC(CH_2)_2Sn(SCH_2\text{-}COOC_8H_{17}\text{-}i)_3$	63438-80-2	3-tris[[2-(isooctyloxy)-2-oxyethyl]thio]-stannylpropanoic acid, butyl ester (10CI)			k,u
$C_{38}H_{74}O_6S_3Sn$	$C_8H_{17}Sn(SCH_2COOC_8H_{17}\text{-}i)_3$	26401-86-5	2,2',2"-[(octylstannylidyne)tris(thio)]-trisacetic acid triisooctyl ester (10CI); octyltin tris(isooctyl thioglycolate)			k,u

Table III-4. (Cont'd)

Empirical formula	Compound	Registry No.	Name	mp(°C)	bp[°C(mmHg)]	Notes
Hydrogen-bound Derivatives						
CH_6Sn	CH_3SnH_3	1631-78-3	methylstannane (10CI); methyltin hydride		0-1.4(760)	
C_2H_8Sn	$C_2H_5SnH_3$	2814-79-1	ethylstannane (8CI); ethyltin hydride		25(760)	
$C_4H_{12}Sn$	$C_4H_9SnH_3$	2406-56-6	butylstannane (10CI); butyltin hydride		98-100(760)	
C_6H_8Sn	$C_6H_5SnH_3$	2406-68-0	phenylstannane (10CI); phenyltin hydride		57-64(106)	
$C_6H_{14}Sn$	$C_6H_{11}SnH_3$	39858-44-1	cyclohexylstannane (10CI); cyclohexyltin hydride			
$C_8H_{20}Sn$	$C_8H_{17}SnH_3$	15232-57-9	octylstannane (10CI); octyltin hydride			

NOTE: All alkyl groups are n-alkyl unless otherwise noted.

a. Biocide used in marine antifouling paint.

b. Wood preservative fungicide.

c. Molluscicide.

d. Methanolysis catalyst.

e. Agrochemical fungicide.

f. Agrochemical insecticide.

g. Disinfectant.

h. Many copolymers are known.

i. Naphth = naphthenyl, i.e. derivative of a naphthenic acid.

j. Additive in glass manufacture.

k. PVC stabilizer.

l. Polyurethane foam catalyst.

m. Feed additive.

n. Esterification catalyst.

o. The homopolymer [32077-00-2] is known as Thermolite 813; Mark OTS.

p. Mixtures of the dibutyl- and monobutyltin derivatives are known as Advastab TM-180; Nuostabe V-1562; V-1902; Ferro 803, 807, 814, 820, 832, 835, 837, 840, 871, 873, 876A, 877; Thermolite 31, 66, 73, 310; Mark 292, 534B, 649A, No. 11, CC-54, CC-78; Advastab TM-220.

q. Possibly incorrectly mentioned in Davies and Smith (1982) as $(CH_3)_2Sn(SC_{11}H_{22})_2$.

r. Mixtures of the composition $(C_4H_9)_2Sn(O(O)CCH{=}CHCOOR)_2$, $R = C_2-C_{12}$, are known as CC-220; Thermolite 25, 26; Mark 275, 693; Advastab T-S2.1, T-150; Ferro 832, 835, 837; Nuostabe V-1525.

s. Stannatrane with no fungicidal activity.

t. Stannatrane with fungicidal activity.

u. Used as mixture of $R_2Sn(IOTG)_2$ and $RSn(IOTG)_3$.

APPENDIX IV.0

Table IV-1. Analytical methods for organotin compounds relevant to aquatic environments (abbreviations used are listed at the end of the table).

No.	Species	Medium	Method	MDA/MDC (Sn)	Comments	Reference
1	$MeSn^{3+}$	$MeSnCl_3$ in Et_2O	Grignard derivatization to $MeBu_3Sn$ or $MeOct_3Sn$, then gc with tcd or hot wire detector			Neubert and Wirth (1975)
2	"	fresh, estuarine, sea-, tap and rainwater	$MeSnH_3$ generation, then flame emission detection (610 nm)	8.40×10^{-14} $mol.L^{-1}$ for 100-mL samples		Braman and Tompkins (1979)
3	"	shells (miscellaneous)	"	8.40×10^{-11} $mol.kg^{-1}$	method of extraction from shells not stated	"
4	"	fresh and seawater	$MeSnH_3$ generation, then quartz tube furnace aas	2.08×10^{-12} mol		Hodge *et al.* (1979)
5	"	$MeSnCl_3$ in organic solvents	hplc-rid		various column packing materials tested	Jessen *et al.* (1979)
6	"	"	(a) gc-hot wire detector, or (b) hplc-rid	(a) could not be determined in presence of Me_4Sn (b) 8.40×10^{-7} mol	(a) redistribution reaction occurs if Me_4Sn is present	Burns *et al.* (1980)
7	"	MeOH/water (97.5/2.5, v/v)	hplc-gfaas		discontinuous method since only part of effluent is sampled, giving nomographic presentation of results; Zr-treated furnaces reduced species-dependent sensitivity	Vickrey *et al.* (1980a)
8	"	$MeSnCl_3$ standards	hplc-rid		acetone-pentane solvent	Glockling (1980)
9	"	"	hplc, then $MeSnH_3$ generation, then electrothermal aas	4.16×10^{-12} mol	no detail given on detector	"
10	"	"	hplc-flame aas	1.60×10^{-10} mol	N_2O-C_2H_2 flame	Burns *et al.* (1981)
11	"	"	gc-aas with quartz tube furnace	9.24×10^{-12} mol	redistribution reaction occurs if Me_4Sn is present	"

Table IV-1. (Cont'd)

No.	Species	Medium	Method	MDA/MDC (Sn)	Comments	Reference
12	$MeSn^{3+}$	$MeSnCl_3$ standards	hplc, then $MeSnH_3$ generation, then aas with quartz tube furnace	6.89×10^{-14} mol		Burns *et al.* (1981)
13	"	water	saturation with NaCl, extraction with tropolone in benzene. Grignard derivatization to $MeBu_3Sn$, then gc-aas with quartz tube furnace	3.36×10^{-10} $mol.L^{-1}$ with 5-L sample		Chau *et al.* (1982)
14	"	$MeSnH_3$	gc-ecd			Mallas *et al.* (1982a)
15	"	estuarine water	generation of $MeSnH_3$ species, then gc-modified-fpd	4.45×10^{-10} $mol.L^{-1}$ with 10-mL samples		Jackson *et al.* (1982)
16	"	marine algae	homogenized, and resulting supernatant analyzed by method No. 4 for $MeSnH_3$			Ishii (1982)
17	"	$MeSnCl_3$ standards	gc-fid	4.16×10^{-10} mol		Tam *et al.* (1983)
18	"	water	$MeSnH_3$ generation, then swept into (a) aas with quartz tube furnace, (b) aas with graphite furnace, or (c) fpd	(a) 5.04×10^{-13} mol (b) 5.04×10^{-13} mol (c) 1.26×10^{-13} mol		Andreae (1983)
19	"	sediment	sonication of dry sediment in HCl or distilled water, followed by method No. 4		no recoveries stated	Tugrul *et al.* (1983)
20	"	limpet shells	dried and homogenized shells sonicated in distilled water, followed by method No. 4		"	"
21	"	fish tissue, macroalgae, soft parts of limpet	homogenized in HCl, followed by method No. 4		"	"

Table IV-1. (Cont'd)

No.	Species	Medium	Method	MDA/MDC (Sn)	Comments	Reference
22	$MeSn^{3+}$	water	see method No. 18	(a) 4.20 x 10^{-13} mol (b) 4.20 x 10^{-13} mol (c) 1.68 x 10^{-13} mol		Andreae and Byrd (1984)
23	Me_2Sn^{2+}	atmosphere above culture media	ms			Huey et al. (1974)
24		Me_2SnCl_2 in Et_2O	method No. 1 with Me_2Bu_2Sn or Me_2Oct_2Sn			Neubert and Wirth (1975)
25	"	fresh, estuarine, sea-, tap and rain-water	Me_2SnH_2 generation, and detection by method No. 2	8.40 x 10^{-14} mol.L^{-1} for 100-mL samples		Braman and Tompkins (1979)
26	"	shells (miscellaneous)	"	8.40 x 10^{-11} mol.kg^{-1}	method of extraction from shells not stated	"
27	"	fresh and sea-water	Me_2SnH_2 generation, then method No. 4	2.27 x 10^{-12} mol		Hodge et al. (1979)
28	"	Me_2SnCl_2 standards	hplc-rid		various column packing materials tested	Jessen et al. (1979)
29	"	"	see method No. 6, (a) and (b)	(a) 6.72 x 10^{-8} mol (b) 7.56 x 10^{-7} mol		Burns et al. (1980)
30	"	Me_2SnCl_2 in MeOH	gfaas	7.56 x 10^{-14} - 1.85 x 10^{-13} mol	Zr-treated furnaces	Vickrey et al. (1980b)
31	"	Me_2SnCl_2 standards	hplc-rid		acetone-pentane solvent	Glockling (1980)
32	"	"	hplc, then Me_2SnH_2 generation, then electrothermal aas	4.54 x 10^{-12} mol	see method No. 9	"
33	"	water	spectrophotometric determination of 3-hydroxyflavone complex		ϵ_{385} = 4.7 x 10^4 L. mol^{-1}.cm^{-1}	Aldridge and Street (1981)
34	"	Me_2SnCl_2 standards	hplc-flame aas	1.43 x 10^{-10} mol	N_2O-C_2H_2 flame	Burns et al. (1981)
35	"	"	gc-aas with quartz tube furnace	8.40 x 10^{-12} mol		"

Table IV-1. (Cont'd)

No.	Species	Medium	Method	MDA/MDC (Sn)	Comments	Reference
36	Me_2Sn^{2+}	Me_2SnCl_2 standards	hplc, then Me_2SnH_2 generation, then aas with quartz tube furnace	7.23 x 10^{-14} mol		Burns et al. (1981)
37	"	"	gc, then Me_2SnH_2 generation and aas with quartz tube furnace	1.26 x 10^{-14} mol		"
38	"	water	method No. 13 with Me_2Bu_2Sn species	3.36 x 10^{-10} mol.L^{-1}, 5-L sample		Chau et al. (1982)
39	"	spent microbiological medium	Me_2SnH_2 derivative analyzed by gc-ecd and gc-ms			Hallas et al. (1982a)
40	"	estuarine water	method No. 15 with Me_2SnH_2 species	1.09 x 10^{-10} mol.L^{-1} with 10-mL samples		Jackson et al. (1982)
41	"	marine algae	method No. 16 for Me_2SnH_2 species			Ishii (1982)
42	"	Me_2SnCl_2 standards	gc-fid	4.54 x 10^{-10} mol		Tam et al. (1983)
43	"	water	Me_2SnH_2 generation, then method No. 18	(a) 5.04 x 10^{-13} mol (b) 5.04 x 10^{-13} mol (c) 1.26 x 10^{-13} mol		Andreae (1983)
44	"	standards	fluorimetric determination of complex with 2',3,4',5,7-pentahydroxyflavone	10^{-9} mol.L^{-1}		Arakawa et al. (1983)
45	"	sediment	sonication of dry sediment in HCl or distilled water, followed by method No. 27		no recoveries stated	Tugrul et al. (1983)
46	"	limpet shells	dried and homogenized shells sonicated in distilled water, followed by method No. 27		"	"
47	"	fish tissue, macroalgae, soft parts of limpet	homogenized in HCl, followed by method No. 27		"	"

Table IV-1. (Cont'd)

No.	Species	Medium	Method	MDA/MDC (Sn)	Comments	Reference
48	Me_2Sn^{2+}	water	see method No. 43	(a) 4.20 x 10^{-13} mol (b) 4.20 x 10^{-13} mol (c) 1.68 x 10^{-13} mol		Andreae and Byrd (1984)
49	Me_3Sn^+	Me_3SnCl standards	gc-fpd	5.01 x 10^{-11} mol	linear response to 5.01 x 10^{-8} mol	Aue and Hill (1972a)
50	"	Me_3SnCl in Et_2O	method No. 1 with Me_3BuSn or Me_3OctSn			Neubert and Wirth (1975)
51	"	fresh, estuarine, sea-, tap and rain-water	Me_3SnH generation and detection by method No. 2	8.40 x 10^{-14} $mol.L^{-1}$, 100-mL samples		Braman and Tompkins (1979)
52	"	Me_3SnCl standards	Me_3SnH generation, then method No. 4	2.00 x 10^{-12} mol		Hodge et al. (1979)
53	"	"	hplc-rid		various column packing materials tested	Jessen et al. (1979)
54	"	"	see method No. 6, (a) and (b)	(a) 6.72 x 10^{-8} mol (b) 6.72 x 10^{-7} mol		Burns et al. (1980)
55	"	MeOH/water (97.5/2.5, v/v)	hplc-gfaas		see method No. 7	Vickrey et al. (1980a)
56	"	Me_3SnCl in MeOH	gfaas	(2.18-4.28) x 10^{-13} mol	Zr-treated furnaces	Vickrey et al. (1980b)
57	"	Me_3SnCl standards	hplc-rid		acetone-pentane solvent	Glockling (1980)
58	"	"	hplc, then Me_3SnH generation, then electrothermal aas	5.01 x 10^{-12} mol	see method No. 9	"
59	"	MeOH	ion exchange hplc-gfaas		possible volatilization during dry and ash cycles	Jewett and Brinckman (1981)
60	"	"	hplc-dppd			MacCrehan (1981)
61	"	water	spectrophotometric determination of 3-hydroxyflavone complex		ε_{385} = 1.5 x 10^4 $L.mol^{-1}.cm^{-1}$	Aldridge and Street (1981)

Table IV-1. (Cont'd)

No.	Species	Medium	Method	MDA/MDC (Sn)	Comments	Reference
62	Me_3Sn^+	Me_3SnCl standards	hplc-flame aas	1.34 x 10^{-10} mol	N_2O-C_2H_2 flame	Burns et al. (1981)
63	"	"	gc-aas with quartz tube furnace	1.01 x 10^{-11} mol		"
64	"	"	hplc, then Me_3SnH generation, then aas with quartz tube furnace	7.98 x 10^{-14} mol		"
65	"	"	gc, then Me_3SnH generation, then aas with quartz tube furnace	1.68 x 10^{-14} mol		"
66	"	water	method No. 13 with Me_3BuSn species	3.36 x 10^{-10} mol.L^{-1}, 5-L sample		Chau et al. (1982)
67	"	spent microbiological medium	Me_3SnH derivative analyzed by gc-ecd and gc-ms			Hallas et al. (1982a)
68	"	estuarine water	method No. 15 with Me_3SnH species	≈8.40 x 10^{-11} mol.L^{-1} for 10-mL samples		Jackson et al. (1982)
69	"	marine algae	method No. 16 for Me_3SnH species			Ishii (1982)
70	"	Me_3SnCl standards	gc-fid	5.01 x 10^{-11} mol		Tam et al. (1983)
71	"	Me_3SnCl in CCl_4 or water	^1H nuclear magnetic resonance spectroscopy			Blunden (1983)
72	"	water	Me_3SnH generation, then method No. 18	(a) 5.04 x 10^{-13} mol (b) 5.04 x 10^{-13} mol (c) 1.26 x 10^{-13} mol		Andreae (1983)
73	"	sediment	sonication of dry sediment in HCl or distilled water, followed by method No. 52		no recoveries stated	Tugrul et al. (1983)

Table IV-1. (Cont'd)

No.	Species	Medium	Method	MDA/MDC (Sn)	Comments	Reference
74	Me_3Sn^+	limpet shells	dried and homogenized shells sonicated in distilled water, followed by method No. 52		no recoveries stated	Tugrul et al. (1983)
75	"	fish tissue, macroalgae, soft parts of limpet	homogenized in HCl, followed by method No. 52		"	"
76	"	water	see method No. 72	(a) 4.20×10^{-13} mol (b) 4.20×10^{-13} mol (c) 1.68×10^{-13} mol		Andreae and Byrd (1984)
77	Me_4Sn	standards	gc with (a) tcd, (b) fid, and (c) gas density balance detectors		relative sensitivities are (a) 1, (b) 1.7 and (c) 10	Pollard et al. (1964)
78	"	"	gc-tcd		determined retention times on 3 stationary phases	Putnam and Pu (1965a)
79	"	"	gc-tcd		extended previous work to temperature programming	Putnam and Pu (1965b)
80	"	"	gc-fpd	5.59×10^{-11} mol	linear response to 5.59×10^{-8} mol	Aue and Hill (1972a)
81	"	"	gc-gfaas	1.01×10^{-10} mol	transfer line maintained at 100°C; graphite furnace run continuously at 1800°C; H_2 added to Ar carrier gas	Parris et al. (1977)
82	"	"	hplc-rid		various column packing materials tested	Jessen et al. (1979)
83	"	"	see method No. 6, (a) and (b)	(a) 6.72×10^{-8} mol (b) 4.20×10^{-7} mol		Burns et al. (1980)
84	"	"	hplc-rid		acetone-pentane solvent	Glockling (1980)
85	"	"	hplc-electrothermal aas	5.59×10^{-12} mol	see method No. 9	"

Table IV-1. (Cont'd)

No.	Species	Medium	Method	MDA/MDC (Sn)	Comments	Reference
86	Me_4Sn	standards	hplc-flame aas	9.24 x 10^{-11} mol	$N_2O-C_2H_2$ flame	Burns et al. (1981)
87	"	"	gc-aas with quartz tube furnace	8.40 x 10^{-12} mol		"
88	"	"	hplc-purge-aas with quartz tube furnace	8.07 x 10^{-14} mol		"
89	"	atmosphere above sediment culture	gc-fid	10^{-7} mol (est.)		Guard et al. (1981)
90	"	standards	gc-ecd and gc-ms			Hallas et al. (1982a)
91	"	estuarine water	purged and trapped, then swept into gc-modified fpd	1.93 x 10^{-10} mol.L^{-1} for 10-mL samples		Jackson et al. (1982)
92	"	standards	gc-fid	5.59 x 10^{-11} mol		Tam et al. (1983)
93	$EtSn^{3+}$	$EtSnCl_3$ standards	see method No. 6, (a) and (b)	(a) 1.34 x 10^{-7} mol (b) 8.40 x 10^{-7} mol		Burns et al. (1980)
94	"	"	hplc-rid		acetone-pentane solvent	Glockling (1980)
95	"	"	hplc, then $EtSnH_3$ generation, then electrothermal aas	3.93 x 10^{-12} mol	see method No. 9	"
96	"	"	hplc-flame aas	1.60 x 10^{-10} mol		Burns et al. (1981)
97	"	"	gc-aas with quartz tube furnace	8.40 x 10^{-12} mol		"
98	"	"	hplc, then $EtSnH_3$ generation, then aas with quartz tube furnace	8.40 x 10^{-14} mol		"
99	"	"	gc, then $EtSnH_3$ generation, then aas with quartz tube furnace	1.85 x 10^{-14} mol		"
100	"	Et_2SnCl_2 standard	Et_2SnH_2 generation, then method No. 4	2.42 x 10^{-12} mol		Hodge et al. (1979)

Table IV-1. (Cont'd)

No.	Species	Medium	Method	MDA/MDC (Sn)	Comments	Reference
101	$EtSn^{3+}$	Et_2SnCl_2 standard	see method No. 6, (a) and (b)	(a) 1.01 x 10^{-7} mol (b) 7.56 x 10^{-7} mol		Burns et al. (1980)
102	Et_2Sn^{2+}	"	hplc-rid		acetone-pentane solvent	Glockling (1980)
103	"	"	hplc, then Et_2SnH_2 generation, then electrothermal aas	4.03 x 10^{-12} mol	see method No. 9	"
104	"	water	spectrophotometric determination of 3-hydroxyflavone complex		ϵ_{385} = 4.1 x 10^4 L. $mol^{-1}.cm^{-1}$	Aldridge and Street (1981)
105	"	Et_2SnCl_2 standards	hplc-flame aas	1.43 x 10^{-10} mol		Burns et al. (1981)
106	"	"	gc-aas with quartz tube furnace	9.24 x 10^{-12} mol		"
107	"	"	hplc, then Et_2SnH_2 generation, then aas with quartz tube furnace	1.01 x 10^{-13} mol		"
108	"	"	gc, then Et_2SnH_2 generation, then aas with quartz tube furnace	3.86 x 10^{-14} mol		"
109	"	"	see method No. 44	10^{-9} $mol.L^{-1}$		Arakawa et al. (1983)
110	Et_3Sn^+	Et_3SnCl standard	Et_3SnH generation, then method No. 4	2.90 x 10^{-12} mol		Hodge et al. (1979)
111	"	"	see method No. 6, (a) and (b)	(a) 6.72 x 10^{-8} mol (b) 6.72 x 10^{-7} mol		Burns et al. (1980)
112	"	"	hplc-rid		acetone-pentane solvent	Glockling (1980)
113	"	"	hplc, then Et_3SnH generation, then electrothermal aas	4.14 x 10^{-12} mol	see method No. 9	"
114	"	MeOH	ion exchange hplc-gfaas		possible volatilization during dry and ash cycles	Jewett and Brinckman (1981)

Table IV-1. (Cont'd)

No.	Species	Medium	Method	MDA/MDC (Sn)	Comments	Reference
115	Et_3Sn^+	MeOH	hplc-dppd			MacCrehan (1981)
116	"	water	spectrophotometric determination of 3-hydroxyflavone complex		ϵ_{385} = 1.1 x 10^4 L. $mol^{-1}.cm^{-1}$	Aldridge and Street (1981)
117	"	Et_3SnCl standards	hplc-flame aas	1.34 x 10^{-10} mol		Burns et al. (1981)
118	"	"	gc-aas with quartz tube furnace	1.01 x 10^{-11} mol		"
119	"	"	hplc, then Et_3SnH generation, then aas with quartz tube furnace	1.13 x 10^{-13} mol		"
120	"	"	gc, then Et_3SnH generation, then aas with quartz tube furnace	4.45 x 10^{-14} mol		"
121	"	"	see method No. 44	5 x 10^{-7} mol.L^{-1}		Arakawa et al. (1983)
122	Et_4Sn	standards	gc-tcd		determined retention times on 3 stationary phases	Putnam and Pu (1965a)
123	"	"	"		extended previous work to temperature programming	Putnam and Pu (1965b)
124	"	"	gc-afid			Dressler et al. (1971)
125	"	"	gc-fid	8.51 x 10^{-14} mol	hydrogen-rich flame; linear response over 10^3X	Aue and Hill (1972b)
126	"	"	gc-fpd	4.25 x 10^{-11} mol	linear response to 4.25 x 10^{-8} mol	Aue and Hill (1972a)
127	"	"	(a) gc-fpd (air-rich) (b) gc-fpd (hydrogen-rich) (c) gc-fid (hydrogen-rich)	(a) 2.13 x 10^{-11} mol (b) 2.13 x 10^{-11} mol (c) 8.51 x 10^{-11} mol		Aue and Hill (1973)
128	"	"	gc-modified-fpd	1.28 x 10^{-13} mol	filterless	Aue and Hastings (1973)

Table IV-1. (Cont'd)

No.	Species	Medium	Method	MDA/MDC (Sn)	Comments	Reference
129	Et_4Sn	standards	see method No. 6, (a) and (b)	(a) 6.72 x 10^{-8} mol (b) 4.20 x 10^{-7} mol		Burns et al. (1980)
130	"	"	gc-modified-fpd	2.10 x 10^{-13} mol (est.)	610-nm optical filter; electronic filter enhanced sensitivity by ≈4X	Kapila and Vogt (1980)
131	"	"	hplc-rid		acetone-pentane solvent	Glockling (1980)
132	"	"	hplc-electrothermal aas	4.25 x 10^{-12} mol	see method No. 9	"
133	"	"	gc-plasma aes			Estes et al. (1980)
134	"	"	hplc-flame aas	9.24 x 10^{-11} mol		Burns et al. (1981)
135	"	"	gc-aas with quartz tube furnace	1.18 x 10^{-11} mol		"
136	"	"	hplc-purge-aas with quartz tube furnace	1.18 x 10^{-13} mol		"
137	"	"	capillary gc-plasma aes	5.04 x 10^{-14} mol	linear range 10^3	Estes et al. (1982)
138	"	MeOH/water (97.5/2.5, v/v)	hplc-gfaas		see method No. 7	Vickrey et al. (1980a)
139	"	MeOH	gfaas	(1.01-1.76) x 10^{-13} mol	Zr-treated furnaces reduced species-dependent sensitivity	Vickrey et al. (1980b)
140	"	water	spectrophotometric determination of 3-hydroxyflavone complex		$\varepsilon_{345} = 4.2 \times 10^4$ L. $mol^{-1}.cm^{-1}$	Aldridge and Street (1981)
141	"	standards	see method No. 44	10^{-9} mol.L^{-1}		Arakawa et al. (1983)
142	Pr_3Sn^+	MeOH	hplc-gfaas			Brinckman et al. (1977)
143	"	"	ion exchange hplc-gfaas		possible volatilization during dry and ash cycles	Jewett and Brinckman (1981)
143a	"	water, sediment	acid extraction into hexane, cleanup on Al_2O_3 column with H_3PO_4, gc-ecd	1.2 x 10^{-9} mol.L^{-1} (water); 6.1 x 10^{-11} mol.g^{-1} (sediment)		Hattori et al. (1984)

Table IV-1. (Cont'd)

No.	Species	Medium	Method	MDA/MDC (Sn)	Comments	Reference
144	Pr_3Sn^+	water	spectrophotometric determination of 3-hydroxyflavone complex		ϵ_{385} = 1.2 x 10^4 L.mol^{-1}.cm^{-1}	Aldridge and Street (1981)
145	"	standards	see method No. 44	5 x 10^{-7} mol.L^{-1}		Arakawa *et al.* (1983)
146	Pr_4Sn	standards	gc-tcd		determined retention times on 3 stationary phases	Putnam and Pu (1965a)
147	"	"	"		extended previous work to temperature programming	Putnam and Pu (1965b)
148	"	"	gc-modified fpd	6.87 x 10^{-16} mol	filterless; linear range 10^3	Aue and Flinn (1977)
149	"	"	gc-modified fpd	2.52 x 10^{-13} mol (est.)	see method No. 130	Kapila and Vogt (1980)
150	"	MeOH	gfaas	(2.94-6.39) x 10^{-13} mol	Zr-treated furnaces reduced species-dependent sensitivity	Vickrey *et al.* (1980b)
151	"	standards	gc-modified fpd	1.37 x 10^{-16} mol	similar to method No. 148, but with quartz wool plug positioned above flame; linear range $>10^3$	Aue and Flinn (1980)
152	"	"	gc-plasma aes			Estes *et al.* (1980)
153	"	standards	capillary gc-plasma aes	5.04 x 10^{-14} mol	linear range 10^3	Estes *et al.* (1982)
154	$BuSn^{3+}$	$BuSnBr_3$ in Et_2O	Grignard conversion to $BuMe_3Sn$, then gc-tcd			Steinmeyer *et al.* (1965)
155	"	standards	Grignard conversion to $BuPr_3Sn$, then gc-tcd			Jitsu *et al.* (1969)
156	"	water	asv	3.4 x 10^{-7} mol.L^{-1}		Woggon *et al.* (1972)

Table IV-1. (Cont'd)

No.	Species	Medium	Method	MDA/MDC (Sn)	Comments	Reference
157	$BuSn^{3+}$	water	extraction with 0.05% tropolone in C_6H_6 or $CHCl_3$, Grignard derivatization to $BuMe_3Sn$, then gc-ms		70-90% recovery at 8.40×10^{-6} mol.L^{-1} level; $BuSn^{3+}$ in water probably adsorbs to glass	Meinema *et al.* (1978)
158	"	fresh water	$BuSnH_3$ generation, then method No. 4	3.18×10^{-12} mol		Hodge *et al.* (1979)
159	Bu_3Sn^+ and inorganic tin	whole fish, viscera, eggs, muscles, and liver	dispersed in conc. HCl; Bu_3Sn^+ and Bu_2Sn^{2+} separated by hexane extraction; hexane-insoluble fraction subjected to wet oxidation; resulting Sn^{4+} extracted into toluene with tropolone and determined by gfaas		procedure does not distinguish $BuSn^{3+}$ from inorganic tin	M & T (1979)
160	"	pure and fresh water	extraction with tropolone in C_6H_6, Grignard derivatization to $BuPe_3Sn$, then gc-modified-fpd	5.68×10^{-13} mol	95-100% recovery from water at 5.68×10^{-5} mol.L^{-1} level	Maguire and Huneault (1981)
161	"	"artificial tap water" extracts of new PVC and CPVC pipe	extraction with tropolone in C_6H_6, Grignard derivatization to $BuPe_3Sn$, then gc-fid	8.52×10^{-9} - 1.70×10^{-8} mol.L^{-1} (1-L samples)		Boettner *et al.* (1981)
162	"	bacterial and fungal cultures	see method No. 157			Baruq (1981)
163	"	estuarine water	method No. 15 with $BuSnH_3$ species	1.51×10^{-10} mol.L^{-1} with 10-mL sample		Jackson *et al.* (1982)
164	"	marine algae	method No. 16 for $BuSnH_3$ species			Ishii (1982)
165	"	benzene	separation from other species by selective halide extraction, then substoichiometric isotope dilution analysis by complexation with salicylidene-amino-2-thiophenol in benzene			Imura and Suzuki (1983)

Table IV-1. (Cont'd)

No.	Species	Medium	Method	MDA/MDC (Sn)	Comments	Reference
166	$BuSn^{3+}$	water	see method No. 160, but with gc-aas with quartz tube furnace	~6.25×10^{-13} mol	sensitivity of fpd and quartz tube furnace aas roughly the same, but aas more stable	Maguire and Tkacz (1983)
167	"	standards	see method No. 44	10^{-7} mol.L^{-1}		Arakawa et al. (1983)
168	"	sediment	dry sediment extracted with tropolone in benzene, then method No. 160	2.84×10^{-8} mol.kg^{-1} with 1-g samples	quantitative recovery in range 5.68×10^{-8} - 5.68×10^{-4} mol.kg^{-1}	Maguire (1984)
169	Bu_2Sn^{2+}	$CHCl_3$	spectrophotometric determination of diphenylcarbazone complex	1.29×10^{-8} mol	can be determined in presence of $BuSn^{3+}$, Bu_3Sn^+ and Bu_4Sn	Skeel and Bricker (1961)
170	"	Bu_2SnBr_2 in Et_2O	Grignard conversion to Bu_2Me_2Sn, then gc-tcd			Steinmeyer et al. (1965)
171	"	standards	Grignard conversion to Bu_2Pr_2Sn, then gc-tcd			Jitsu et al. (1969)
172	"	seawater	extraction with CCl_4, oxidation to Sn^{4+}, then spectrophotometric determination of phenylfluorone complex	5.68×10^{-8} mol.L^{-1}		Mor et al. (1973)
173	"	water	method No. 157 with Bu_2Me_2Sn		70-90% recovery at 8.40×10^{-6} mol.L^{-1} level	Meinema et al. (1978)
174	"	fish, muscles, and liver	dispersed in conc. HCl, extracted with hexane, complexed with tropolone and cleaned up with an acid wash. The hexane layer is analyzed by gfaas for total Bu_3Sn^+ and Bu_2Sn^{2+}. The hexane layer is then extracted with NaOH to remove Bu_2Sn^{2+} and analyzed again by gfaas for Bu_3Sn^+. Bu_2Sn^{2+} is determined by difference		recoveries not stated	M & T (1979)

Table IV-1. (Cont'd)

No.	Species	Medium	Method	MDA/MDC (Sn)	Comments	Reference
175	Bu_2Sn^{2+}	whole fish, viscera and eggs	as per method No. 174, but analytes subjected to wet oxidation to Sn^{4+} before gfaas		oxidation removes lipid interference; recoveries not stated	M & T (1979)
176	"	fresh water	Bu_2SnH_2 generation, then method No. 4	3.29 x 10^{-12} mol		Hodge et al. (1979)
177	"	MeOH/water (97.5/2.5, v/v)	hplc-gfaas		see method No. 7	Vickrey et al. (1980a)
178	"	MeOH	gfaas	(1.09-1.85) x 10^{-13} mol	Zr-treated furnaces reduced species-dependent sensitivity	Vickrey et al. (1980b)
179	"	soil	extraction with wet Et_2O/formic acid (98/2, v/v), tlc and scintillation counting		70% recovery	Barug and Vonk (1980)
180	"	water	spectrophotometric determination of 3-hydroxyflavone complex		ϵ_{385} = 4.0 x 10^4 L.mol^{-1}.cm^{-1}	Aldridge and Street (1981)
181	"	pure and fresh water	method No. 160 with Bu_2Pe_2Sn	5.15 x 10^{-13} mol	>95% recovery at 4.29 x 10^{-5} mol.L^{-1}	Maguire and Huneault (1981)
182	"	"	see method No. 161, with Bu_2Pe_2Sn species	6.44 x 10^{-9} - 1.29 x 10^{-8} mol.L^{-1}		Boettner et al. (1981)
183	"	bacterial and fungal cultures	see method No. 173			Barug (1981)
184	"	estuarine water	method No. 15 with Bu_2SnH_2 species	3.11 x 10^{-10} mol.L^{-1} with 10-mL samples		Jackson et al. (1982)
185	"	fishing nets	dppd	6.2 x 10^{-8} mol.L^{-1}		Hasebe et al. (1982)
186	"	air	collection with glass fiber filter and XAD-2 resin, extraction with 1% HOAc/MeCN, then hplc-gfaa with Zr-treated L'vov platforms		satisfactory in range 8.40 x 10^{-5} - 1.68 x 10^{-3} mol.L^{-1}	Gutknecht et al. (1982)
187	"	benzene	method No. 165			Imura and Suzuki (1983)

Table IV-1. (Cont'd)

No.	Species	Medium	Method	MDA/MDC (Sn)	Comments	Reference
188	Bu_2Sn^{2+}	standards	method No. 44	10^{-9} mol. L^{-1}		Arakawa et al. (1983)
189	"	water	see method No. 166, with Bu_2Pe_2Sn species	(5.15-6.01) x 10^{-13} mol	see method No. 166	Maguire and Tkacz (1983)
190	"	sediment	see method No. 168, with Bu_2Pe_2Sn species	2.14 x 10^{-8} mol. kg^{-1} with 1-g samples	see method No. 168	Maguire (1984)
191	Bu_3Sn^{+}	standards	Grignard conversion to Bu_3PrSn, then gc-tcd			Jitsu et al. (1969)
192	"	seawater	method No. 172	4.29 x 10^{-8} mol.L^{-1}		Mor et al. (1973)
193	"	50% (v/v) EtOH	dppd	3.2 x 10^{-7} mol.L^{-1}		Fleet and Fouzder (1975)
194	"	acidic aqueous solution	asv after dealkylation under UV light	~6.9 x 10^{-8} mol. L^{-1}		Woggon and Jehle (1975)
195	"	MeOH	hplc-gfaas			Brinckman et al. (1977)
196	"	Bu_3SnH standards	gc-modified fpd	3.44 x 10^{-15} mol	see method No. 148	Aue and Flinn (1977)
197	"	water	extraction with 0.05% tropolone in C_6H_6 or $CHCl_3$, Grignard derivatization to Bu_3MeSn, then gc-ms		70-90% recovery at 8.40 x 10^{-6} mol.L^{-1} level	Meinema et al. (1978)
198	"	soil	radiolabelled compound extracted with acetic acid, partitioned into hexane, then tlc and scintillation counting		% recovery not stated	Sheldon (1978)
199	"	standards	Bu_3SnH generation, then method No. 4	6.14 x 10^{-12} mol		Hodge et al. (1979)
200	"	fish, muscles and liver	see method No. 174		recoveries not stated	M & T (1979)
201	"	whole fish, viscera and eggs	see method No. 175		see method No. 175	"

Table IV-1. (Cont'd)

No.	Species	Medium	Method	MDA/MDC (Sn)	Comments	Reference
202	Bu_3Sn^+	water (spiked)	extracted with hexane, oxidized with H_2SO_4-H_2O_2, then spectrophotometric determination of phenylfluorone complex	8.40×10^{-10} mol	linear response to 3.36×10^{-9} mol	Sherman and Carlson (1980)
203	"	MeOH	gfaas	6.72×10^{-14} - 1.85×10^{-13} mol	Zr-treated furnaces reduced species-dependent sensitivity	Vickrey et al. (1980b)
204	"	soil	see method No. 179		% recovery not stated	Barug and Vonk (1980)
205	"	MeOH	ion-exchange hplc-gfaas	$\leq 4.20 \times 10^{-11}$ mol		Jewett and Brinckman (1981)
206	"	"	hplc-dppd			MacCrehan (1981)
207	"	water	spectrophotometric determination of 3-hydroxyflavone complex		$\varepsilon_{385} = 1.2 \times 10^4$ L. mol^{-1}.cm^{-1}	Aldridge and Street (1981)
208	"	pure and fresh water	method No. 160 with Bu_3PeSn	5.17×10^{-13} mol	>96% recovery at 3.45×10^{-5} mol.L^{-1} level	Maguire and Huneault (1981)
209	"	"artificial tap water" extracts of new PVC and CPVC pipe	see method No. 161, with Bu_3PeSn species	5.17×10^{-9} - 1.03×10^{-8} mol.L^{-1}		Boettner et al. (1981)
210	"	bacterial and fungal cultures	see method No. 197			Barug (1981)
211	"	fishing nets	dppd	2.2×10^{-7} mol.L^{-1}		Hasebe et al. (1982)
212	"	estuarine bacterial cultures	cells collected by centrifugation, then HNO_3 oxidation, then gfaas			Blair et al. (1982)
213	"	bound to bacterial cells	cells centrifuged, extracted with MeOH, then ion-exchange hplc-gfaas			"
214	"	air	see method No. 186		see method No. 186	Gutknecht et al. (1982)

Table IV-1. (Cont'd)

No.	Species	Medium	Method	MDA/MDC (Sn)	Comments	Reference
215	Bu_3Sn^+	seawater	dpasv	≈3.45 x 10^{-8} mol.L^{-1}		Kenis and Zirino (1983)
216	"	benzene	method No. 165			Imura and Suzuki (1983)
217	"	standards	see method No. 44	5 x 10^{-7} mol.L^{-1}		Arakawa et al. (1983)
218	"	water	see method No. 160, with Bu_3PeSn species	5.17 x 10^{-13} mol		Maguire and Tkacz (1983)
219	"	sediment	see method No. 168, with Bu_3PeSn species	1.73 x 10^{-8} mol. kg^{-1} with 1-g samples	see method No. 168	Maguire (1984)
220	TBTO	air	glass fiber filters extracted with MIBK, then flame-aas	5.17 x 10^{-13} mol		Jeltes (1969)
221	Bu_4Sn	standards	gc-tcd			Steinmeyer et al. (1965)
222	"	"	"		determined retention times on 3 stationary phases	Putnam and Pu (1965a)
223	"	"	"		extended previous work to temperature programming	Putnam and Pu (1965b)
224	"	"	"			Jitsu et al. (1969)
225	"	"	gc-fpd	2.88 x 10^{-11} mol	linear response to 2.88 x 10^{-8} mol	Aue and Hill (1972a)
226	"	"	gc-modified fpd	2.88 x 10^{-15} mol	see method No. 148	Aue and Flinn (1977)
227	"	"	gc-modified fpd	5.76 x 10^{-15} mol	see method No. 130	Kapila and Vogt (1980)
228	"	MeOH	gfaas	(1.26-1.93) x 10^{-13} mol	Zr-treated furnaces reduced species-dependent sensitivity	Vickrey et al. (1980b)
229	"	air	see method No. 186		see method No. 186	Gutknecht et al. (1982)
230	$OctSn^{3+}$	standards	Grignard conversion to $OctPe_3Sn$, then gc-tcd			Jitsu et al. (1969)

Table IV-1. (Cont'd)

No.	Species	Medium	Method	MDA/MDC (Sn)	Comments	Reference
231	$OctSn^{3+}$	standards	Grignard conversion to $OctMe_3Sn$, then gc with tcd or hot wire detector			Neubert and Wirth (1975)
232	"	"	Grignard conversion to $OctEt_3Sn$, then gc-tcd			Figge et al. (1977)
233	"	water	asv	3.4 x 10^{-7} mol.L^{-1}		Woggon et al. (1972)
234	Oct_2Sn^{2+}	standards	Grignard conversion to Oct_2Pe_2Sn, then gc-tcd			Jitsu et al. (1969)
235	"	"	Grignard conversion to Oct_2Me_2Sn, then gc with tcd or hot wire detector			Neubert and Wirth (1975)
236	"	"	Grignard conversion to Oct_2Et_2Sn, then gc-tcd			Figge et al. (1977)
237	Oct_3Sn^+	standards	Grignard conversion to Oct_3PeSn, then gc-tcd			Jitsu et al. (1969)
238	"	"	Grignard conversion to Oct_3MeSn, then gc with tcd or hot wire detector			Neubert and Wirth (1975)
239	"	"	Grignard conversion to Oct_3EtSn, then gc-tcd			Figge et al. (1977)
240	$CySn^{3+}$	residues on apples and pears	fruit extracted with HOAc/hexane solution, which was in turn extracted with HCl and back-extracted with hexane; $CySn^{3+}$ in the HCl phase was oxidized to Sn^{4+} and determined spectrophotometrically as dithiol complex			Getzendaner and Corbin (1972)
241	"	$CySnBr_3$ standards	gc-cd		on-column degradation	Gauer et al. (1974)

Table IV-1. (Cont'd)

No.	Species	Medium	Method	MDA/MDC (Sn)	Comments	Reference
242	$CySn^{3+}$	on glass slides and wax-coated glass slides	tlc with spot identification by diphenylthiocarbazone and quantitation by scintillation counting of the radio-labelled spike			Smith _et_ _al_. (1976)
243	Cy_2Sn^{2+}	residues on apples and pears	start with method No. 240; Cy_2Sn^{2+} in back-extracted hexane solution transferred to KOH solution, back-extracted with hexane and analyzed as in method No. 240			Getzendaner and Corbin (1972)
244	"	residues on strawberries, apples and grapes, and in water	extracted with C_6H_6, converted by HBr to Cy_2SnBr_2, cleaned up and analyzed by gc-cd		80-90% recovery from fruit at 3.32×10^{-7} - 3.32×10^{-6} mol.L^{-1} level; 94% recovery from water at 3.32×10^{-6} mol.L^{-1}; on-column degradation or adsorption noted	Gauer _et_ _al_. (1974)
245	"	on glass slides and wax-coated glass slides	see method No. 242			Smith _et_ _al_. (1976)
246	"	MeOH/water (97.5/2.5, v/v)	hplc-gfaas		see method No. 7	Vickrey _et_ _al_. (1980a)
247	"	MeOH	gfaas	(1.09-2.02) $\times 10^{-13}$ mol	Zr-treated furnaces reduced species-dependent sensitivity	Vickrey _et_ _al_. (1980b)
248	Cy_3Sn^{+}	residues on fruit	wet oxidation to Sn^{4+}, then spectrophotometric determination of dithiol complex	1.68×10^{-6} mol		Corbin (1970)
249	"	residues on apples and pears	start with method No. 243, Cy_3Sn^{+} in the hexane solution after KOH extraction is oxidized to Sn^{4+} and analyzed by method No. 240			Getzendaner and Corbin (1972)

Table IV-1. (Cont'd)

No.	Species	Medium	Method	MDA/MDC (Sn)	Comments	Reference
250	Cy_3Sn^+	residues on strawberries, apples and grapes, and in water	extracted with C_6H_6, converted by HBr to Cy_3SnBr, cleaned up and analyzed by gc-cd		78-95% recovery from fruit at $2.60 \times 10^{-7} - 2.60 \times 10^{-6}$ mol.L^{-1} level; 99% recovery from water at 2.60×10^{-6} mol.L^{-1}; on-column degradation or adsorption noted	Gauer et al. (1974)
251	"	on glass slides and wax-coated glass slides	see method No. 242			Smith et al. (1976)
252	"	standards	Grignard conversion to Cy_3PhSn, then gc-fid		Grignard reaction catalyzed by CuCl; yield >95% linear response from $1.12 \times 10^{-10} - 6.74 \times 10^{-9}$ mol	Esposto et al. (1978)
253	"	"	Grignard conversion to Cy_3MeSn or Cy_3EtSn, then gc-ms			Stewart and Cannizzaro (1980)
254	"	MeOH	ion-exchange-hplc-gfaas	$<4.20 \times 10^{-11}$ mol		Jewett and Brinckman (1981)
255	"	as Cy_3SnOH in air	filter samples wet ashed, then Sn^{4+} determined by gfaas			Houk and Beaulieu (1981)
256	"	air	see method No. 186		see method No. 186	Gutknecht et al. (1982)
257	$PhSn^{3+}$	standards	Grignard conversion to $PhPe_3Sn$, then gc-tcd			Jitsu et al. (1969)
258	"	on glass plate (after photolysis)	detection by tlc with catechol violet spray; quantitation by oxidation to Sn^{4+} followed by spectrophotometric determination of phenylfluorone complex			Chapman and Price (1972)
259	"	"	tlc with UV-fluorescence		qualitative	Barnes et al. (1973)
260	"	standards	fluorescence determination of 3-hydroxyflavone complex		λ_{ex} = 470 nm, λ_{em} = 490 nm	Vernon (1974)

Table IV-1. (Cont'd)

No.	Species	Medium	Method	MDA/MDC (Sn)	Comments	Reference
261	$PhSn^{3+}$	water	extracted with tropolone in $CHCl_3$, determined spectrophotometrically with a number of complexing agents, or by gc-fid as $PhSnCl_3$		low yield implied for conversion to $PhSnCl_3$	Freitag and Bock (1974a)
262	"	on sugar beet leaves and in rats (radio-labelled Ph_3Sn^+ spike)	see method No. 261 with scintillation counting			Freitag and Bock (1974b)
263	"	standards	fluorescence determination of 3-hydroxyflavone complex		complex is unstable under laboratory light; λ_{ex} = 415 nm; λ_{em} = 450 nm	Blunden and Chapman (1978)
264	"	water	extracted with CH_2Cl_2, transferred to hexane, $PhSnH_3$ generated and analyzed by gc-ecd		poor recoveries	Soderquist and Crosby (1978)
265	"	standards	$PhSnH_3$ generation, then method No. 4	3.30 x 10^{-12} mol		Hodge et al. (1979)
266	"	"	Grignard conversion to $PhMe_3Sn$, then gc-fpd		"nearly quantitative" conversion; no optical filter	Wright et al. (1979)
267	"	spiked in estuarine water	method No. 15 with $PhSnH_3$ species	1.93 x 10^{-10} mol. L^{-1} with 10-mL samples		Jackson et al. (1982)
268	Ph_2Sn^{2+}	standards	Grignard conversion to Ph_2Pe_2Sn, then gc-tcd			Jitsu et al. (1969)
269	"	on glass plate (after photolysis)	see method No. 258			Chapman and Price (1972)
270	"	"	see method No. 259		qualitative	Barnes et al. (1973)
271	"	standards	fluorescence determination of 3-hydroxyflavone complex		λ_{ex} = 465 nm, λ_{em} = 495 nm	Vernon (1974)

Table IV-1. (Cont'd)

No.	Species	Medium	Method	MDA/MDC (Sn)	Comments	Reference
272	Ph_2Sn^{2+}	water	extracted with a number of complexing agents in different organic solvents and determined spectrophotometrically with a number of complexing agents, or by gc-fid as Ph_2SnCl_2		low yield implied for conversion to Ph_2SnCl_2	Freitag and Bock (1974a)
273	"	on sugar beet leaves and in rats (radio-labelled Ph_3Sn^+ spike)	see method No. 272 with scintillation counting			Freitag and Bock (1974b)
274	"	standards	fluorescence determination of 3-hydroxyflavone complex		see method No. 263	Blunden and Chapman (1978)
275	"	water	see method No. 264 with Ph_2SnH_2		poor recoveries	Soderquist and Crosby (1978)
276	"	standards	Grignard conversion to Ph_2Me_2Sn, then gc-fpd		"nearly quantitative" conversion; no optical filter	Wright et al. (1979)
277	Ph_3Sn^+	standards	Grignard conversion to Ph_3PeSn, then gc-tcd			Jitsu et al. (1969)
278	"	potatoes	extraction with MeCN, then asv	10^{-8} mol.L^{-1} for pure standards		Booth and Fleet (1970)
279	"	on glass plates	see method No. 258			Chapman and Price (1972)
280	"	seawater	method No. 172	3.98×10^{-8} mol.L^{-1}		Mor et al. (1973)
281	"	soil (radio-labelled spike)	extracted with hot organic solvents, then scintillation counting		recoveries diminished with soil-contact time	Barnes et al. (1973)
282	"	standards	fluorescence determination of 3-hydroxyflavone complex	1.34×10^{-9} mol	λ_{ex} = 415 nm, λ_{em} = 497 nm	Vernon (1974)

Table IV-1. (Cont'd)

No.	Species	Medium	Method	MDA/MDC (Sn)	Comments	Reference
283	Ph_3Sn^+	water	extracted with $CHCl_3$ or CH_2Cl_2 with spectrophotometric determination of dithizone complex, or by gc-fid as Ph_3SnCl			Freitag and Bock (1974a)
284	"	on sugar beet leaves and in rats (radio-labelled spike)	see method No. 283 with scintillation counting			Freitag and Bock (1974b)
285	"	50% (v/v) EtOH	dppd	10^{-7} mol.L^{-1}		Fleet and Fouzder (1975)
286	"	acidic aqueous solution	asv after dealkylation under UV light	2.44 x 10^{-11} mol.L^{-1}		Woggon and Jehle (1975)
287	"	MeOH	hplc-gfaas			Brinckman et al. (1977)
288	"	standards	Grignard conversion to Ph_4Sn, then gc-fid		Grignard reaction catalyzed by CuCl; yield >95%; linear response from 1.17 x 10^{-10} - 7.02 x 10^{-9} mol	Esposto et al. (1978)
289	"	distilled, tap, canal and synthetic seawater (spiked)	extracted with toluene, then fluorescence determination of 3-hydroxyflavone complex		λ_{ex} = 415 nm, λ_{em} = 495 nm; recoveries varied from 94% at 5.19 x 10^{-6} mol.L^{-1} to 74% at 1.04 x 10^{-8} mol.L^{-1}	Blunden and Chapman (1978)
290	"	water	see method No. 264 with Ph_3SnH		quantitative recovery at 1.43 x 10^{-7} mol.L^{-1}	Soderquist and Crosby (1978)
291	"	soil	radiolabelled compound extracted with acetic acid, partitioned into hexane, then tlc and scintillation counting		% recovery not stated	Sheldon (1978)
292	"	standards	Grignard conversion to Ph_3MeSn, then gc-fpd	2.85 x 10^{-14} mol	linear response to 100 ng; "nearly quantitative" conversion; no optical filter	Wright et al. (1979)

Table IV-1. (Cont'd)

No.	Species	Medium	Method	MDA/MDC (Sn)	Comments	Reference
293	Ph_3Sn^+	seaweeds with radiolabelled spike	seaweed digested with a quaternary ammonium hydroxide in toluene, then scintillation counting			Callow *et al.* (1979)
294	"	*Daphnia magna* in water with radiolabelled Ph_3Sn^+	dissolved *Daphnia* in HNO_3, neutralized, then scintillation counting			Filenko and Isakova (1979)
295	"	MeOH/water (97.5/2.5, v/v)	hplc-gfaas		see method No. 7	Vickrey *et al.* (1980a)
296	"	MeOH	gfaas	(1.09-1.60) x 10^{-13} mol		Vickrey *et al.* (1980b)
297	"	standards	Grignard conversion to Ph_3MeSn or Ph_3EtSn, then gc-ms			Stewart and Cannizzaro (1980)
298	"	soil	extraction as Ph_3SnCl with CH_2Cl_2, transfer to acetone, then gc-ms			Kuwahara *et al.* (1980)
299	"	MeOH	ion-exchange-hplc-gfaas	<4.20 x 10^{-4} mol		Jewett and Brinckman (1981)
300	"	"	hplc-dppd		linear response from 10^{-4} - 10^{-6} mol.L^{-1}	MacCrehan (1981)
301	"	water	spectrophotometric determination of 3-hydroxyflavone complex		ϵ_{385} = 1.5 x 10^4 L. $mol^{-1}.cm^{-1}$	Aldridge and Street (1981)
302	"	Ph_3SnCl standards	flame aas		air/H_2 flame; comparisons made with other flames and atomic emission	Marr and Anwar (1982)
303	"	standards	see method No. 44	10^{-7} mol.L^{-1}		Arakawa *et al.* (1983)
304	Ph_4Sn	standards	gc-fpd	2.34 x 10^{-15} mol	see method No. 148	Aue and Flinn (1977)
305	"	"	gc-fpd	2.34 x 10^{-14} mol	no optical filter	Wright *et al.* (1979)

Table IV-1. (Cont'd)

No.	Species	Medium	Method	MDA/MDC (Sn)	Comments	Reference
306	Ph_4Sn	MeOH/water (97.5/2.5, v/v)	hplc-gfaas		see method No. 7	Vickrey *et al.* (1980a)
307	"	MeOH	gfaas	6.72 x 10^{-14} - 1.51 x 10^{-13} mol		Vickrey *et al.* (1980b)
308	"	toluene	size exclusion chromatography with icp-aes		method also used for Vi_4Sn and two phenyl organotin compounds containing acetylenic bonds	Hausler and Taylor (1981)
309	"	standards	flame aas		air/H_2 flame; comparisons made with other flames and atomic emission; method also used for Vi_4Sn, hexaphenylditin and a number of uncommon organotin compounds with Sn-S-phenyl linkages	Marr and Anwar (1982)
310	Vendex	apples, oranges and tea leaves	homogenize, extract with Et_2O/HOAC, clean up on silica gel column, then gfaas	4.75 x 10^{-12} mol	can also determine two degradation products, tetrakis(2-methyl-2-phenylpropyl)-distannoxane and 2-methyl-2-phenylpropyl stannoic acid	Sano *et al.* (1979)
311	"	standards	Grignard conversion to methyltri-(2-methyl-2-phenylpropyl)tin; then gc-ms			Stewart and Cannizzaro (1980)

Abbreviations are as follows:

aas	atomic absorption spectrometry
aes	atomic emission spectroscopy
afid	alkaline flame ionization detector
Ar	argon
asv	anodic stripping voltammetry
Bu	butyl
C_2H_2	acetylene
C_6H_6	benzene
CH_2Cl_2	dichloromethane
$CHCl_3$	chloroform
CCl_4	carbon tetrachloride
cd	Coulson conductivity detector
CPVC	chlorinated poly(vinyl chloride)
Cy	cyclohexyl
dpasv	differential pulse anodic stripping voltammetry
dppd	differential pulse polarographic detector
ecd	electron capture detector
edl	electrodeless discharge lamp
Et	ethyl
EtOH	ethyl alcohol
EtOAc	ethyl acetate
Et_2O	diethyl ether
fid	flame ionization detector
fpd	flame photometric detector
gc	gas chromatography
gc-ms	gas chromatography - mass spectrometry
gfaas	graphite furnace atomic absorption spectrometry
H_2	hydrogen
HCl	hydrochloric acid
HNO_3	nitric acid
HOAc	acetic acid
hplc	high-pressure liquid chromatography
i	iso-
icp-aes	inductively coupled plasma - atomic emission spectroscopy
ir	infrared
MDA	minimum detectable amount
MDC	minimum detectable concentration
Me	methyl
MeCN	acetonitrile
MeOH	methanol
MHz	megahertz
MIBK	methylisobutylketone
ms	mass spectrometry
N_2O	nitrous oxide
NaOH	sodium hydroxide
naa	neutron activation analysis
Oct	octyl
Pe	pentyl
Ph	phenyl
Pr	propyl
PVC	poly(vinyl chloride)
rbp	reverse bonded phase
rid	refractive index detector
tcd	thermal conductivity detector
TBTO	bis(tributyltin) oxide
tlc	thin-layer chromatography
UV	ultraviolet
Vendex	hexakis(2-methyl-2-phenylpropyl)distannoxane
Vi	vinyl

APPENDIX V.0

Table V-1. Aquatic environmental occurrence of tin and organotin compounds.

Species	Medium	Concentration (mol.L^{-1} Sn or mol.kg^{-1} Sn)	Location	Reference
total Sn	seawater	6.81×10^{-9}	Pacific Ocean	Hamaguchi *et al.* (1964)
	marine animals	1.43×10^{-5}	Tokyo Bay (*Metapenaeus joyneri*, *Watosenia scintillans* and *Meretrix meretrix cusoria*)	"
	estuarine water	$(1.68\text{-}3.36) \times 10^{-10}$	general	Smith and Burton (1972)
	shelf water	"	"	"
	surface Atlantic water	7.56×10^{-11}	"	"
	drinking water	n.d. - 2.52×10^{-7}	general	WHO (1980)
		$(4.20\text{-}10.92) \times 10^{-11}$		Braman and Tompkins (1979)
	fresh water	n.d. - 6.13×10^{-9}	Florida	"
		$(2.52\text{-}7.56) \times 10^{-7}$	N.O. polder, Netherlands	Leeuwangh *et al.* (1976)
		"	Delft, Netherlands	"
		$<8.40 \times 10^{-9}$ - 1.43×10^{-7}	Malaysia	Peterson *et al.* (1976)
		3.36×10^{-11}	general	Iverson and Brinckman (1978)
	estuarine water	8.40×10^{-11} - 4.87×10^{-9}	Florida	Braman and Tompkins (1979)
		$<1.68 \times 10^{-8}$	Chesapeake Bay, U.S.A.	Hallas and Cooney (1981a)
		1.68×10^{-9} - 1.68×10^{-7}	Baltimore Harbor, U.S.A.	Jackson *et al.* (1982)
		$(1.85\text{-}3.28) \times 10^{-8}$	Malaysia	Peterson *et al.* (1976)
	seawater	7.56×10^{-11}	North Atlantic Ocean (average)	Iverson and Brinckman (1978)

Table V-1. (Cont'd)

Species	Medium	Concentration (mol.L^{-1} Sn or mol.kg^{-1} Sn)	Location	Reference
total Sn	seawater	2.10 x 10^{-8}	Malaysia	Peterson et al. (1976)
		2.52 x 10^{-8}	general	WHO (1980)
		1.68 x 10^{-11} - 7.14 x 10^{-10}	Florida	Braman and Tompkins (1979)
	rainwater	3.36 x 10^{-11} - 3.78 x 10^{-10}	Florida	"
	sewage treatment plant outfall	1.28 x 10^{-6}	Chesapeake Bay, U.S.A.	Hallas and Cooney (1981a)
	sediment	8.40 x 10^{-6} - 1.68 x 10^{-4} (dry weight)	Narragansett Bay, U.S.A.	Hodge et al. (1979)
		n.d. - 8.40 x 10^{-4} (dry weight)	Lake Leman, Switzerland	Dogan and Haerdi (1980)
		8.40 x 10^{-6} - 3.36 x 10^{-5}	N.O. polder, Netherlands	Leeuwangh et al. (1976)
		1.68 x 10^{-5}	Delft, Netherlands	"
		2.02 x 10^{-3}	Baltimore Harbor	Hallas and Cooney (1981a)
		6.72 x 10^{-6} - 6.64 x 10^{-5}	Chesapeake Bay	"
		6.72 x 10^{-5} - 3.78 x 10^{-3}	Germany	Schramel et al. (1973)
		4.20 x 10^{-6} - 1.18 x 10^{-4} (dry weight)	Savannah River estuary, U.S.A.	Seidel et al. (1980)
		8.40 x 10^{-6} - 2.10 x 10^{-4} (dry weight)	Lake Michigan	"
		6.72 x 10^{-5} - 2.44 x 10^{-4} (dry weight)	Palace moat, Tokyo	"
		n.d. - 1.51 x 10^{-5} (dry weight)	Mission Bay, San Diego, U.S.A.	"

Table V-1. (Cont'd)

Species	Medium	Concentration (mol.L^{-1} Sn or mol.kg^{-1} Sn)	Location	Reference
total Sn	sediment	1.68 x 10^{-5} at 55 cm core depth, roughly constant to 20 cm, then increasing to 2.18 x 10^{-4} at 4 cm depth	Lake Michigan	Goldberg et al. (1981)
	municipal sewage sludges	9.33 x 10^{-4} - 4.13 x 10^{-3} (dry weight)	U.S.A.	Furr et al. (1976)
	thallophytes (primarily algae and "plankton")	(2.52-4.20) x 10^{-5} (dry weight)	Lake Leman, Switzerland	Dogan and Haerdi (1980)
		(4.20-9.24) x 10^{-6} (dry weight)	St. Vincent's Gulf, Australia	Maher (1982)
		2.52 x 10^{-7} - 9.24 x 10^{-6} (dry weight)	California	Hodge et al. (1979)
		(1.26-2.69) x 10^{-5}	Gulf of Naples, Italy	Smith (1970)
	embryophytes (largely terrestrial plants and macrophytes)	3.36 x 10^{-5} - 1.08 x 10^{-4} (dry weight)	Lake Leman, Switzerland	Dogan and Haerdi (1980)
		1.68 x 10^{-6} - 1.26 x 10^{-5} (dry weight)	Germany	Schramel et al. (1973)
		1.26 x 10^{-5} - 2.69 x 10^{-4} (dry weight)	Malaysia	Peterson et al. (1976)
		7.06 x 10^{-5} - 1.82 x 10^{-2} (dry weight)	Malaysia (near Sn smelter)	"
	coelenterates	1.01 x 10^{-5}	Gulf of Naples, Italy	Smith (1970)
	pelecypods (molluscs, oysters)	<8.40 x 10^{-8} (dry weight)	St. Vincent's Gulf, Australia	Maher (1982)

Table V-1. (Cont'd)

Species	Medium	Concentration ($mol.L^{-1}$ Sn or $mol.kg^{-1}$ Sn)	Location	Reference
total Sn	pelecypods (molluscs, oysters)	$2.52 \times 10^{-7} - 1.05 \times 10^{-5}$ (dry weight)	Lake Michigan	Goldberg *et al.* (1981)
		$<1.26 \times 10^{-6} - 7.98 \times 10^{-6}$ (wet weight)	France	Alzieu *et al.* (1980)
		$7.14 \times 10^{-6} - 9.24 \times 10^{-4}$	"	Alzieu *et al.* (1982)
		$<2.52 \times 10^{-7} - 1.34 \times 10^{-5}$	Gulf of Naples, Italy	Smith (1970)
	gastropods	$1.68 \times 10^{-7} - 1.09 \times 10^{-6}$	N.O. polder, Netherlands	Leeuwangh *et al.* (1976)
	crustaceans	$5.04 \times 10^{-7} - 2.52 \times 10^{-5}$	Gulf of Naples, Italy	Smith (1970)
	insects	3.36×10^{-7}	N.O. polder, Netherlands	Leeuwangh *et al.* (1976)
	echinoderms	$<2.52 \times 10^{-7} - 8.07 \times 10^{-6}$	Gulf of Naples, Italy	Smith (1970)
	tunicates	$4.20 \times 10^{-6} - 1.26 \times 10^{-4}$	"	"
	osteichthyes (fish)	$<8.40 \times 10^{-8} - 1.68 \times 10^{-7}$ (dry weight)	St. Vincent's Gulf, Australia	Maher (1982)
		$3.36 \times 10^{-6} - 7.06 \times 10^{-8}$ (dry weight)	Lake Leman, Switzerland	Dogan and Haerdi (1980)
		$(1.60-5.29) \times 10^{-3}$	N.O. polder, Netherlands	Leeuwangh *et al.* (1976)
		$(1.93-4.28) \times 10^{-4}$	Delft, Netherlands	"
		n.d. - 5.04×10^{-6} (dry weight)	Germany	Schramel *et al.* (1973)
		$<2.52 \times 10^{-7}$	Gulf of Naples, Italy	Smith (1970)
Inorganic Sn	drinking water	1.68×10^{-11}	Florida	Braman and Tompkins (1979)

Table V-1. (Cont'd)

Species	Medium	Concentration (mol.L^{-1} Sn or mol.kg^{-1} Sn)	Location	Reference
Inorganic Sn	fresh water	$<2.52 \times 10^{-12} - 6.13 \times 10^{-9}$	Florida	Braman and Tompkins (1979)
↓		$7.06 \times 10^{-10} - 4.12 \times 10^{-9}$	Lake Michigan, U.S.A.	Hodge *et al*. (1979)
		n.d. - 1.04×10^{-9}	rivers in south-eastern U.S.A	Byrd and Andreae (1982)
		1.55×10^{-10}	Rhine River, Germany	"
		1.01×10^{-10}	Main River, Germany	"
		n.d. - 4.20×10^{-7}	Ontario	Maguire *et al*. (1982)
	fresh water surface microlayer	n.d. - 5.32×10^{-6}	"	"
	estuarine water	$<2.52 \times 10^{-12} - 4.76 \times 10^{-9}$	Florida	Braman and Tompkins (1979)
	"	$1.68 \times 10^{-9} - 1.68 \times 10^{-7}$	Baltimore Harbor	Jackson *et al*. (1982)
	seawater	$<2.52 \times 10^{-12} - 5.21 \times 10^{-10}$	Florida	Braman and Tompkins (1979)
		$2.52 \times 10^{-12} - 3.19 \times 10^{-10}$	California	Hodge *et al*. (1979)
		$2.52 \times 10^{-11} - 6.53 \times 10^{-8}$	La Jolla, California	Tugrul *et al*. (1983)
	coastal sea-water	$(3.3-4.5) \times 10^{-11}$	Saanich Inlet, B.C.	Lu and Thompson (1983)
	rainwater	$2.52 \times 10^{-11} - 3.44 \times 10^{-10}$	Florida	Braman and Tompkins (1979)
		$8.40 \times 10^{-12} - 2.52 \times 10^{-11}$	La Jolla, California	Tugrul *et al*. (1983)
		4.20×10^{-11}		"
	sediment	$6.72 \times 10^{-7} - 4.31 \times 10^{-8}$ (dry weight)	Ontario	Maguire (1984)

Table V-1. (Cont'd)

Species	Medium	Concentration ($mol.L^{-1}$ Sn or $mol.kg^{-1}$ Sn)	Location	Reference
Inorganic Sn	sediment	n.d. - 9.24×10^{-5} (dry weight)	California coast	Seidel et al. (1980)
	shell samples	$<4.20 \times 10^{-10}$ - 2.44×10^{-8}	Florida	Braman and Tompkins (1979)
	invertebrates	$(1.18\text{-}4.37) \times 10^{-7}$ (dry weight)	San Diego Bay, California	Seidel et al. (1980)
	algae	n.d. - 1.07×10^{-5} (dry weight)	"	"
		$(1.34\text{-}9.83) \times 10^{-7}$ (dry weight)	San Francisco Bay	"
		$(1.53\text{-}7.66) \times 10^{-9}$ (wet weight)	Mission Bay, California	Ishii (1982)
		4.21×10^{-9} - 5.75×10^{-8} (wet weight)	San Diego Bay	"
	smelt and trout	$(1.41\text{-}5.20) \times 10^{-6}$	Ontario	Chau et al. (1984)
$MeSn^{3+}$	drinking water	4.20×10^{-12} - 6.81×10^{-11}	Florida	Braman and Tompkins (1979)
	fresh water	$<8.40 \times 10^{-14}$ - 1.01×10^{-10}	"	"
		$(2.49\text{-}7.90) \times 10^{-11}$	Lake Michigan	Hodge et al. (1979)
		n.d. - 1.18×10^{-11}	rivers in southeastern U.S.A.	Byrd and Andreae (1982)
		5.92×10^{-10}	Rhine River, Germany	"
		5.04×10^{-10} - 1.01×10^{-8}	Ontario	Maguire et al. (1982)
	estuarine water	$<8.40 \times 10^{-14}$ - 7.14×10^{-11}	Florida	Braman and Tompkins (1979)
	seawater	$<8.40 \times 10^{-14}$ - 1.26×10^{-10}	"	"

Table V-1. (Cont'd)

Species	Medium	Concentration (mol.L^{-1} Sn or mol.kg^{-1} Sn)	Location	Reference
$MeSn^{3+}$	seawater	n.d. - 3.33×10^{-11}	California	Hodge *et al*. (1979)
	rainwater	n.d. - 8.40×10^{-11}	La Jolla, California	Tugrul *et al*. (1983)
	seawater	n.d. - 3.53×10^{-10}		"
	sediment	n.d. - 8.91×10^{-8} (dry weight)	general	"
	fish (*U. moluccensis*)	2.27×10^{-7} (dry weight)		"
	smelt and trout	2.44×10^{-7} - 3.40×10^{-6}	Ontario	Chau *et al*. (1984)
	limpet (*Patella caerulea*)	3.36×10^{-9} - 4.03×10^{-8} (dry weight)		"
	seaweed	1.41×10^{-7} (dry weight		"
	rainwater	5.04×10^{-12} - 1.85×10^{-11}	Florida	Braman and Tompkins (1979)
	shell samples	<8.40×10^{-11} - 3.78×10^{-9}	"	"
	algae	n.d. - 1.66×10^{-9} (wet weight)	Mission Bay, California	Ishii (1982)
		n.d. - 4.99×10^{-9} (wet weight)	San Diego Bay	"
Me_2Sn^{2+}	drinking water	3.36×10^{-12} - 1.85×10^{-11}	Florida	Braman and Tompkins (1979)
	fresh water	<8.40×10^{-14} - 6.30×10^{-11}	"	"
		n.d. - 2.86×10^{-10}	Lake Michigan	Hodge *et al*. (1979)
		n.d. - 2.61×10^{-11}	rivers in southeastern U.S.A.	Byrd and Andreae (1982)

Table V-1. (Cont'd)

Species	Medium	Concentration ($mol.L^{-1}$ Sn or $mol.kg^{-1}$ Sn)	Location	Reference
Me_2Sn^{2+}	fresh water	1.77×10^{-9}	Rhine River, Germany	Byrd and Andreae (1982)
		3.4×10^{-12}	Main River, Germany	"
		n.d. - 3.36×10^{-9}	Ontario	Maguire *et al.* (1982)
	estuarine water	5.88×10^{-12} - 3.86×10^{-11}	Florida	Braman and Tompkins (1979)
		$<4.20 \times 10^{-11}$ - 4.12×10^{-9}	Baltimore Harbor	Jackson *et al.* (1982)
	seawater	5.04×10^{-12} - 5.88×10^{-11}	Florida	Braman and Tompkins (1979)
		n.d. - 2.04×10^{-10}	California	Hodge *et al.* (1979)
	rainwater	$<8.40 \times 10^{-14}$ - 6.22×10^{-11}	Florida	Braman and Tompkins (1979)
	shell samples	$<8.40 \times 10^{-11}$ - 1.76×10^{-9}	"	"
	algae	n.d. - 1.00×10^{-8} (dry weight)	San Diego Bay	Seidel *et al.* (1980)
		n.d. - 9.09×10^{-10} (wet weight)	Mission Bay, California	Ishii (1982)
		1.82×10^{-9} - 1.00×10^{-8} (wet weight)	San Diego Bay	"
	seawater	n.d. - 3.78×10^{-10}		Tugrul *et al.* (1983)
	sediment	n.d. - 1.13×10^{-7} (dry weight)		"
	fish (*U. moluccensis* and *M. barbatus*)	$\sim 2.31 \times 10^{-8}$ (dry weight)		"
	trout	n.d. - 1.49×10^{-7}	Ontario	Chau *et al.* (1984)

Table V-1. (Cont'd)

Species	Medium	Concentration (mol.L^{-1} Sn or mol.kg^{-1} Sn)	Location	Reference
Me_2Sn^{2+}	limpet (*Patella caerulea*)	1.68 x 10^{-9} - 1.51 x 10^{-7} (dry weight)		Tugrul *et al.* (1983)
	brown macro-algae	4.20 x 10^{-9} (dry weight)		"
	chlorophytes	1.01 x 10^{-7} (dry weight)		"
	seaweed	3.11 x 10^{-7} (dry weight)		"
Me_3Sn^+	drinking water	4.20 x 10^{-12} - 2.02 x 10^{-11}	Florida	Braman and Tompkins (1979)
	fresh water	<8.40 x 10^{-14} - 6.39 x 10^{-11}	"	"
		n.d. - 4.20 x 10^{-10}	Ontario	Maguire *et al.* (1982)
		n.d. - 1.43 x 10^{-11}	rivers in southeastern U.S.A.	Byrd and Andreae (1982)
		1.35 x 10^{-11}	Rhine River, Germany	"
		2.5 x 10^{-12}	Main River, Germany	"
	estuarine water	<8.40 x 10^{-14} - 3.36 x 10^{-11}	Florida	Braman and Tompkins (1979)
		<4.20 x 10^{-11} - 1.68 x 10^{-10}	Baltimore Harbor	Jackson *et al.* (1982)
	seawater	<8.40 x 10^{-14} - 8.23 x 10^{-12}	Florida	Braman and Tompkins (1979)
	rainwater	<8.40 x 10^{-14} - 9.24 x 10^{-12}	"	"
	shell samples	<8.40 x 10^{-11}	"	"
	algae	n.d. - 1.50 x 10^{-9} (wet weight)	San Diego Bay	Ishii (1982)

Table V-1. (Cont'd)

Species	Medium	Concentration ($mol.L^{-1}$ Sn or $mol.kg^{-1}$ Sn)	Location	Reference
Me_3Sn^+	sediment	n.d. - 1.63×10^{-7} (dry weight)		Tugrul *et al.* (1983)
	fish (*U. moluccensis* and *M. barbatus*)	≈1.05×10^{-8} (dry weight)		"
	limpet (*Patella caerulea*)	5.88×10^{-9} - 5.29×10^{-7} (dry weight)		"
	brown macroalgae	4.87×10^{-8} (dry weight)		"
	seaweed	7.56×10^{-9} (dry weight)		"
Me_4Sn	estuarine water	<8.40×10^{-11} - 2.52×10^{-9}	Baltimore Harbor	Jackson *et al.* (1982)
	invertebrates	n.d. - 3.35×10^{-8}	California coast	Seidel *et al.* (1980)
	algae	n.d. - 6.98×10^{-8} (dry weight)	San Diego Bay	"
		n.d. - 6.93×10^{-8} (dry weight)	San Francisco Bay	"
		n.d. - 5.59×10^{-8} (wet weight)	San Diego Bay	Ishii (1982)
$BuSn^{3+}$	fresh water	7.79×10^{-11} - 4.32×10^{-9}	Lake Michigan	Hodge *et al.* (1979)
		n.d. - 4.83×10^{-8}	Ontario	Maguire *et al.* (1982)
	estuarine water	n.d. - 1.68×10^{-9}	Baltimore Harbor	Jackson *et al.* (1982)
	sediment	n.d. - 3.29×10^{-6} (dry weight)	Ontario	Maguire (1984)

Table V-1. (Cont'd)

Species	Medium	Concentration (mol.L^{-1} Sn or mol.kg^{-1} Sn)	Location	Reference
$BuSn^{3+}$	sediment	n.d. - 4.35×10^{-8} (dry weight)	California coast	Seidel *et al*. (1980)
	algae	present, but not quantitated	Mission and San Diego Bays	Ishii (1982)
Bu_2Sn^{2+}	fresh water	3.29×10^{-11} - 5.26×10^{-9}	Lake Michigan	Hodge *et al*. (1979)
		n.d. - 3.13×10^{-8}	Ontario	Maguire *et al*. (1982)
	fresh water surface micro-layer	n.d. - 1.11×10^{-5}	"	"
	sediment	n.d. - 1.50×10^{-6} (dry weight)	"	Maguire (1984)
Bu_3Sn^{+}	fresh water	n.d. - 1.00×10^{-8}	"	Maguire *et al*. (1982)
	fresh water surface micro-layer	n.d. - 2.09×10^{-7}	"	"
	sediment	n.d. - 1.86×10^{-6} (dry weight)	"	Maguire (1984)
Me_2SnH_2	estuarine water	$<4.20 \times 10^{-11}$ - 4.20×10^{-10}	Baltimore Harbor	Jackson *et al*. (1982)
$BuSnH_3$	estuarine water	$(4.20\text{-}8.40) \times 10^{-10}$	"	"
Bu_2Me_2Sn	sediment	n.d. - 4.68×10^{-8} (dry weight)	Ontario	Maguire (1984)
Bu_3MeSn	sediment	n.d. - 7.47×10^{-8} (dry weight)	"	"

APPENDIX VI.0

Table VI-0. Abundance of tin by lithologic category and four sedimentary domains (from Horn and Adams 1966).

A Computed abundance of tin by lithologic category ($mg.kg^{-1}$)

Igneous	Shale	Sandstone	Carbonate	Evaporite	Oceanic clay	Oceanic carbonate
2.49	4.12	0.115	0.166	-	2.40	0.402

B Computed abundance of tin for the four sedimentary domains ($mg.kg^{-1}$)

Continent-shield	Mobile-belt shelf	Hemipelagic	Pelagic
2.24	2.47	2.20	2.12

C Mass distribution within domains[α]

Continent-shield	Mobile-belt shelf	Hemi-pelagic	Pelagic	Connate water	Sea-water	Weathered igneous
0.00574	0.0190	0.0164	0.00969	4.40×10^{-6}[β]	42.1×10^{-6}[β]	0.0508

[α] In units of geograms (10^{20} g = 1 geogram)

[β] These values based upon data available in 1965.

APPENDIX VII.0

Table VII-1. Properties and transformations of inorganic tin and organotin compounds relevant to aquatic environmental fate.

Species	Medium	Transformation/ property	Half-life	Comments	Reference
Sn(II)	pure water	oxidation to Sn^{4+}	~2 d	23°C	Fanchiang and Wood (1981)
	lake water/ sediment	methylation to $MeSn^{3+}$, Me_2Sn^{2+} and Me_3Sn^+		20°C; 10-14 d; yields <0.004%	Chau *et al.* (1981)
	pure water	methylation by MeI to $MeSn^{3+}$, Me_2Sn^{2+} and Me_3Sn^+		19°C; 5 d; yields <0.4%	"
Sn(IV)	nutrient medium	bacterial production of Me_2Sn^{2+}		Me_2Sn^{2+} identification tentative; used tin-tolerant *Pseudomonas* strain; partially anaerobic conditions; no yield stated	Huey *et al.* (1974)
	"	bacterial production of Me_4Sn and a methyltin hydride more volatile than Me_4Sn		Used tin-tolerant *Pseudomonas* strain; aerobic; 2 weeks at 23°C; no yield stated; the Me_4Sn may have resulted from chemical decomposition of a methyltin hydride	Jackson *et al.* (1982)
	lake water/ sediment	methylation to $MeSn^{3+}$, Me_2Sn^{2+} and Me_3Sn^+		20°C; 10-14 d; yields <0.008%	Chau *et al.* (1981)
	nutrient medium/ sediment	methylation to Me_2Sn^{2+} and Me_3Sn^+		25°C; 14 d; positive identification, but no yields stated	Hallas *et al.* (1982a)
$MeSn^{3+}$	lake water/ sediment	methylation to Me_2Sn^{2+}		20°C; 10-14 d; yield = 2.6%	Chau *et al.* (1981)
	CCl_4	UV photolysis to Sn^{4+}	7 h	$\lambda \geq 235$ nm	Blunden (1983)
	pure water	"	1500 h (est.)	$\lambda \geq 200$ nm	"
Me_2Sn^{2+}	lake water/ sediment	methylation to Me_3Sn^+		20°C; 10-14 d; yield = 11.4%	Chau *et al.* (1981)

Table VII-1. (Cont'd)

Species	Medium	Transformation/ property	Half-life	Comments	Reference
Me_2Sn^{2+}	CCl_4	UV photolysis to $MeSn^{3+}$	3 h	λ ≥ 235 nm	Blunden (1983)
	pure water	UV photolysis	300 h (est.)	λ ≥ 200 nm; SnO_2 detected, but not $MeSn^{3+}$	"
Me_3Sn^+	seawater/ sediment	production of Me_4Sn		2.4% yield after 80 d at 16°C; autoclaved controls also produce (less) Me_4Sn; mechanism may be disproportionation	Guard *et al.* (1981)
	lake water/ sediment	production of Me_4Sn		20°C; 10-14 d; yield = 0.0008%	Chau *et al.* (1981)
	"	demethylation to Me_2Sn^{2+} and $MeSn^{3+}$		20°C; 10-14 d; yields 0.3 and 0.9%, respectively	"
	CCl_4	UV photolysis to Me_2Sn^{2+}	2 h	λ ≥ 235 nm	Blunden (1983)
	pure water	UV photolysis to Me_2Sn^{2+}	30 h	λ ≥ 200 nm	"
Me_3SnOH [or $(Me_3Sn)_2O$]	neat	reaction with atmospheric CO_2		production of $(Me_3Sn)_2CO_3$ in substantial yield	Brown *et al.* (1972)
Et_2Sn^{2+}	pure water	persistence	2 d	products not stated; reaction is described, without elaboration, as "hydrolysis"	Mazayev *et al.* (1976)
	pond water	"	1.5 d	"	"
	pond water/ mud	"	2.5 d	"	"
	pure water	UV photolysis	1.7 d	wavelength not stated, nor are products; reaction is described, without elaboration, as "hydrolysis"	"

Table VII-1. (Cont'd)

Species	Medium	Transformation/ property	Half-life	Comments	Reference
Et_3Sn^+	fish	uptake by carp		accumulation principally in liver, brain, spinal cord, kidneys and red muscles	Stroganov et al. (1973)
Et_3SnOH [or $(Et_3Sn)_2O$]	neat	reaction with atmospheric CO_2		production of $(Et_3Sn)_2CO_3$ in substantial yield	Brown et al. (1972)
Pr_3Sn^+	nutrient medium	uptake by E. coli		uptake apparently the result of reaction with phospholipids and other phosphorus-containing compounds in cell walls	Yamada et al. (1978)
Pr_3SnOH [or $(Pr_3Sn)_2O$]	neat	reaction with atmospheric CO_2		production of $(Pr_3Sn)_2CO_3$ in substantial yield	Brown et al. (1972)
$BuSn^{3+}$	seawater	solubility		9-10 $mg.L^{-1}$	Meinema et al. (1978)
	90% H_2O (v/v) - 10% MeOH	ultraviolet spectrum		λ, nm (ε, $L.mol^{-1}.cm^{-1}$): 360 (0.07); 350 (0.08); 340 (0.10); 330 (0.23); 320 (0.54); 310 (1.21); 300 (2.38); 290 (3.53); 280 (3.73)	Maguire et al. (1983)
	90% H_2O (v/v) - 10% MeCN	photolysis at 300 nm	0.4 ± 0.1 d	Sn^{4+} produced in 68% yield	"
Bu_2Sn^{2+}	seawater	solubility		6-8 $mg.L^{-1}$	Meinema et al. (1978)
	90% H_2O (v/v) - 10% MeOH	ultraviolet spectrum		λ, nm (ε, $L.mol^{-1}.cm^{-1}$): 360 (0.03); 350 (0.04); 340 (0.05); 330 (0.06); 320 (0.07); 310 (0.10); 300 (0.16); 290 (0.29); 280 (0.75)	Maguire et al. (1983)
	90% H_2O (v/v) - 10% MeCN	photolysis at 300 nm	>9 d	small amounts of $BuSn^{3+}$ and Sn^{4+} produced	"
	12% HCl	photolysis	<1 h	wavelength not stated; dealkylation eventually to Sn^{4+}	Woggon and Jehle (1975)

Table VII-1. (Cont'd)

Species	Medium	Transformation/ property	Half-life	Comments	Reference
Bu_2Sn^{2+}	pure water	persistence	1.1 d	products not stated; reaction is described, without elaboration, as "hydrolysis"	Mazayev et al. (1976)
	pond water	"	1.6 d	"	"
	pond water/mud	"	1.1 d	"	"
	pond water/sand	"	1.3 d	"	"
	pure water	UV photolysis	0.8 d	wavelength not stated, nor are products; reaction is described, without elaboration, as "hydrolysis"	"
	benzene/methanol	"	<6 d	wavelength not stated	Akagi and Sakagami (1971)
	fungal culture medium	"	~14 d	$BuSn^{3+}$ identified as product upon aerobic incubation of Coniophora puteana; 30°C	Barug (1981)
	solutions of reducing sugars in phosphate buffers	"	~1 d	$BuSn^{3+}$ major product	"
	lake water/ sediment	production of Me_3Sn^+		20°C; 10-14 d; yield 0.002%	Chau et al. (1981)
Bu_3Sn^+	pure water	log K_{ow}		3.2 at pH 6 and 20°C	Maguire et al. (1983)
	"	adsorption to glass and Teflon		significant below 2 mg.L^{-1}	"
	"	volatilization		none over 62 d at 20°C	"
	"	stability in dark		no loss of butyl groups from tin over 63 d at 20°C between pH 2.9 and 10.3	"

Table VII-1. (Cont'd)

Species	Medium	Transformation/ property	Half-life	Comments	Reference
Bu_3Sn^+	90% H_2O (v/v) - 10% MeOH	ultraviolet spectrum		λ, nm (ε, $L.mol^{-1}.cm^{-1}$): 360 (0.06); 350 (0.10); 340 (0.16); 330 (0.26); 320 (0.40); 310 (0.64); 300 (0.98); 290 (1.62); 280 (2.72)	Maguire *et al.* (1983)
	pure water	photolysis at 300 nm	1.1 ± 0.2 d	products: Bu_2Sn^{2+}, $BuSn^{3+}$ and Sn^{4+}; product yield ≈50%	"
	"	photolysis at 300 nm, sensitized with 15 $mg.L^{-1}$ fulvic acid	0.6 ± 0.2 d		"
	"	photolysis at 350 nm	>18 d		"
	"	photolysis at 350 nm, sensitized with 15 $mg.L^{-1}$ fulvic acid	6.2 ± 1.8 d		"
	fresh water or distilled water	sunlight photolysis	>89 d (>4 x 10^4 langleys)	small amounts of Bu_2Sn^{2+}, $BuSn^{3+}$ and Sn^{4+} formed	"
	12% HCl	photolysis	<1 h	wavelength not stated; dealkylation eventually to Sn^{4+}	Woggon and Jehle (1975)
	plant surfaces	photolysis	≈4 h	Bu_2Sn^{2+}, $BuSn^{3+}$ and Sn^{4+} produced; wavelength not stated	"
	12% HCl	dealkylation		solution boiled; no product yield or kinetics given	"
	pure water	reaction with MeI		19°C; 5 d; products were $MeSn^{3+}$ (8 x 10^{-5}%), Me_2Sn^{2+} (2 x 10^{-5}%) and Me_3Sn^+ (8 x 10^{-5}%)	Chau *et al.* (1981)
	"	persistence	19 d	products not stated; reaction is described, without elaboration, as "hydrolysis"	Mazayev *et al.* (1976)

Table VII-1. (Cont'd)

Species	Medium	Transformation/ property	Half-life	Comments	Reference
Bu_3Sn^+	tap water	chemical stability	>16 d	its chemical stability was defined as the length of time its molluscicidal activity remained unchanged when it was dissolved in tap water at a concentration close to the 24-h LC_{90} value for (unidentified) snails. The container used was made of wax-lined paper	Ritchie and Berrios-Duran (1969)
	fresh water	stability	>3 months		Woggon and Jehle (1975)
	seawater	reaction with CO_2 to form $(Bu_3Sn)_2CO_3$		claim made with no supporting evidence on yield or kinetics; no references given	Sheldon (1975)
	pond water	persistence	10.5 d	products not stated; reaction is described, without elaboration, as "hydrolysis"	Mazayev et al. (1976)
	pond water/sand	"	3.8 d	"	"
	fresh water and seawater (pH 5-9)	stability in dark		little or no loss of butyl groups from tin over 35 d. Solubility limit exceeded in some tests. Possibility of adsorption to glass container walls	Slesinger and Dressler (1978)
	water	photolysis under General Electric F40BL fluorescent lights	18.5 d (bis-(tributyltin) oxide) 2 d (tributyltin fluoride)	half-life varied with source of Bu_3Sn^+, and was considerably shorter in the presence of acetone photosensitizer; the light source used approximates the spectral distribution of sunlight, but the relative intensities are unknown	"
	lake water/ sediment	production of Me_3Sn^+		20°C; 10-14 d; yield 0.002%	Chau et al. (1981)

Table VII-1. (Cont'd)

Species	Medium	Transformation/ property	Half-life	Comments	Reference
Bu_3Sn^+	soil	dealkylation (aerobic)	15-20 weeks	20°C in the dark; $^{14}CO_2$ and Bu_2Sn^{2+} among products; considerable formation of unextractable residues	Barug and Vonk (1980)
	soil (clay, sand and top soil)	leaching from soil		little leaching after 16 weeks (2.5 cm of rain per week); little experimental detail given	Schatzberg and Harris (1978)
	soil	"	>180 d	25°C; substantial production of Bu_2Sn^{2+} and $BuSn^{3+}$. Substantial unextractable residue	Sheldon (1978)
	"	dissipation (aerobic)	≈60 d	combination of (at least) dealkylation and formation of unextractable residues	"
	"	dealkylation (anaerobic)	>180 d	25°C; substantial production of Bu_2Sn^{2+} and $BuSn^{3+}$. Substantial unextractable residue	"
	"	dissipation (anaerobic)	<200 d	combination of (at least) dealkylation and formation of unextractable residues	"
	impregnated in wood posts	mobility in terrestrial microcosm		93.6% ^{14}C radiolabel retained in wood, 4.5% in surrounding soil, indicating very little migration after 2.5 months. Earthworms accumulated 7.9 $mg.kg^{-1}$ from the soil, indicating that soil-associated residues were not biologically unavailable; however, no evidence presented to show that the radiolabel is unequivocably Bu_3Sn^+	Gile *et al.* (1982)

Table VII-1. (Cont'd)

Species	Medium	Transformation/ property	Half-life	Comments	Reference
Bu_3Sn^+	culture medium	dealkylation	5-10 d	*Pseudomonas aeruginosa* in aerobic medium degraded Bu_3Sn^+ to $BuSn^{3+}$; no Bu_2Sn^{2+} detected, perhaps because Bu_2Sn^{2+} was quickly converted to $BuSn^{3+}$ by reducing sugars in phosphate buffer	Barug (1981)
	"	"	3-4 d	*Coniophora puteana* in aerobic medium effects the transformation $Bu_3Sn^+ \rightarrow Bu_2Sn^{2+} \rightarrow BuSn^{3+}$	"
	"	uptake by estuarine bacteria		Bu_3Sn^+ accumulated to 3.7-7.7 mg $Sn.g^{-1}$ dry weight of cells, probably by simple adsorption to cell walls; no dealkylation noted	Blair *et al.* (1982)
	"	accumulation and dealkylation by a green alga	4 weeks	*Ankistrodesmus falcatus* had a maximum apparent algal bioconcentration factor of 3×10^4; over 40 weeks at 20°C, 50% of the original Bu_3Sn^+ was converted to Bu_2Sn^{2+} and small quantities of $BuSn^{3+}$ and Sn^{4+}	Maguire *et al.* (1984)
	sheepshead minnow (*Cyprinodon variegatus*)	uptake and dealkylation		maximum observed bioconcentration factor for whole fish was 2.6×10^3. Depuration "first half-life" was 7 d. Metabolism to Bu_2Sn^{2+}, $BuSn^{3+}$ and Sn^{4+}	Ward *et al.* (1981)
Bu_3OH [or $(Bu_3Sn)_2O$]	neat	reaction with atmospheric CO_2		production of $(Bu_3Sn)_2CO_3$ in substantial yield	Brown *et al.* (1972)
$(Bu_3Sn)_2O$	seawater	solubility		8-10 $mg.L^{-1}$	Meinema *et al.* (1978)

Table VII-1. (Cont'd)

Species	Medium	Transformation/ property	Half-life	Comments	Reference
$(Bu_3Sn)_2O$	pure water	solubility		0.7-7 mg.L^{-1} at 20°C and pH 5-7, increasing with both increasing and decreasing pH	Maguire et al. (1983)
	neat	vapor pressure		6.7 x 10^{-7} mmHg at 20°C; estimated by a kinetic comparative technique	"
	neat	UV photolysis		wavelength not stated; irradiation for 24 h at 24°C; products were 1-butene and traces of polymeric Bu_2SnO and aldehydes	Komora and Popl (1978)
Oct_2Sn^{2+}	pure water	persistence	3.2 d	products not stated; reaction is described, without elaboration, as "hydrolysis"	Mazayev et al. (1976)
	pond water	"	6.2 d	"	"
	pond water/mud	"	1.9 d	"	"
	pond water/sand	"	4.7 d	"	"
	benzene/methanol	"	<15 d	wavelength not stated	Akagi and Sakagami (1971)
$CySn^{3+}$	water	photolysis		wavelength not stated; cyclohexanone and cyclohexanol were prominent products	Casida et al. (1971)
Cy_2Sn^{2+}	"	"		"	"
	neat (as Cy_2SnO), on glass plates	volatilization		10% loss over 100 d	Smith et al. (1976)
Cy_3Sn^+	water	photolysis		wavelength not stated; cyclohexane and cyclohexanol were prominent products	"

Table VII-1. (Cont'd)

Compound	Medium	Transformation/ Property	Half-life	Comments	Reference
Cy_3Sn^+	on apples and pears	persistence	<5 weeks	products were Cy_2Sn^{2+}, $CySn^{3+}$ and Sn^{4+}; some loss by rain; very little translocation of residue from surface to the insides of apples and pears	Getzendaner and Corbin (1972)
	soil	dealkylation		orchards treated with Plictran for up to 3 years had residues consisting of 80% Cy_3Sn^+, 14% Cy_2Sn^{2+} and 6% $CySn^{3+}$; there was little leaching from soil since the residue was found almost entirely in the 0-15 cm layer	Blair (1975)
	on glass plates and on "apple wax"	photolysis	≈8 h	corresponds roughly to 8 d irradiation in a sunny climate. Reaction pathway appears to be by sequential dealkylation; 80% conversion to Sn^{4+} over 32 d	Smith _et_ _al_. (1976)
	neat (as Cy_3SnOH), on glass plates	volatilization		none over 100 d	"
	pure water	"		evidence for "co-distillation" with water	"
$PhSn^{3+}$	water	stability	several minutes	at $[PhSn^{3+}]_0 > 4$ mg.L^{-1}, 80-90% recovery of Sn^{4+}; at $[PhSn^{3+}]_0 < 0.1$ mg.L^{-1}, Sn^{4+} accounted for only 10% of the products; evidence for production of water-soluble polymeric tin species	Soderquist and Crosby (1978)
Ph_2Sn^{2+}	water	stability	2-3 d	21°C, pH 5.5-8.5; no $PhSn^{3+}$ or Sn^{4+} produced; no wall adsorption	Soderquist and Crosby (1980)

Table VII-1. (Cont'd)

Species	Medium	Transformation/ property	Half-life	Comments	Reference
Ph_2Sn^{2+}	5% aqueous acetone	sensitized sunlight photolysis	≈5 h	acetone photosensitizer; the dark control was also unstable (see above); evidence for production of water-soluble polymeric tin species	Soderquist and Crosby (1980)
Ph_3Sn^+	TLC plates	sunlight photolysis	<8 h		Cenci and Cremonini (1969)
	soils	degradation	<3 d	no evidence that they were not simply measuring adsorption to soil	"
	benzene/methanol	UV photolysis	≈17 d	λ not stated	Akagi and Sakagami (1971)
	glass plate	UV photolysis		products were Ph_2Sn^{2+}, $PhSn^{3+}$ and Sn^{4+}	Chapman and Price (1972)
	soil	binding		strong binding indicated by 50% decrease in extractability over 40 d from sterile or non-sterile soil. Little leaching from soil with water	Barnes *et al.* (1973)
	silica gel plates	UV photolysis		$\lambda > 254$ nm; degradation to Sn^{4+} via Ph_2Sn^{2+} and $PhSn^{3+}$	"
	soil	degradation	≈140 d	50% of ^{14}C label evolved as $^{14}CO_2$ over 140 d from non-sterile soil	"
	culture medium	"		$^{14}CO_2$ released by *Aspergillus* sp. conidia and a Gram-negative bacterium	"
	soil	degradation	>9 weeks	degradation products not identified; no translocation by hop or oat roots	Suess and Eben (1973)

Table VII-1. (Cont'd)

Species	Medium	Transformation/ property	Half-life	Comments	Reference
Ph_3Sn^+	on sugar beet leaves exposed to sunlight but protected from rain	dealkylation	$\approx$14 d	production of Ph_2Sn^{2+}, $PhSn^{3+}$ and Sn^{4+}; significant amounts of unextractable ^{113}Sn residue	Freitag and Bock (1974b)
	12% HCl	UV photolysis	<10 min	wavelength not stated; dealkylation eventually to Sn^{4+}	Woggon and Jehle (1975)
	soil	persistence	1 d	first half-life 1 d, second half-life $\approx$6 d; no products identified; may simply have been observing strong binding to soil	Kuwahara _et_ _al_. (1980)
	lake water/ sediment	production of Me_3Sn^+		20°C; 10-14 d; yield 0.002%	Chau _et_ _al_. (1981)
	fresh water and seawater (pH 5-9)	stability in dark		no loss of Ph_3Sn^+ over 35 d at pH 5-7 and in seawater; 43% loss at pH 9	Slesinger and Dressler (1978)
	water	photolysis under General Electric F40BL fluorescent lights	54 d	$t_{\frac{1}{2}}$ = 12.5 d in presence of acetone photosensitizer; the light source used approximates the spectral distribution of sunlight, but the relation intensities are unknown	"
	"	stability		no loss of Ph_3Sn^+ over 30 d at pH 4.2-10.0 and 21-32°C	Soderquist and Crosby (1980)
	"	volatilization		none over 6 d at 32°C even though the water loss from the test beakers was 55 $mL.d^{-1}$	"

Table VII-1. (Cont'd)

Species	Medium	Transformation/ property	Half-life	Comments	Reference
Ph_3Sn^+	water	photolysis (sunlight)	14-21 d	pH 7.2; similar results with a laboratory photoreactor ($\lambda >$ 290 nm, $t_{\frac{1}{2}} = 14$ d); the photolysis was accelerated considerably by acetone and rose bengal ($t_{\frac{1}{2}} < 1$ d), but not by filtered rice-field water; evidence for mechanism featuring production to Ph_2Sn^+ accompanied by further degradation to water-soluble polymeric tin species	Soderquist and Crosby (1980)

REFERENCES

Abe, K., Suzuki, S. and Nose, H. (Inventors.) 1973. Imparting flame-resistance to plastics. Tokyo Fine Chemical Co., Ltd., assignee. Japan Patent 32,770. 1973 October 9. 10 pp.

Abo-Elghar, M.R. and Radwan, H. 1971. Toxicological, chemosterilant and histopathological effects of triphenyltin hydroxide on *Spodoptera littoralis* Boisd. Acta Phytopathol. Acad. Sci. Hung. 6(1-4): 261-280.

Agriculture Canada. 1984. Compendium of pest control products registered in Canada. Accessible through the COMSHARE database.

Akagi, H. and Sakagami, Y. 1971. On degradation of organotin compounds by ultra violet ray. Koshu Eiseiin Kenkyu Hokoku (Bull. Inst. Public Health (Jpn.)) 20(1): 1-4. (In Japanese.)

Alabaster, J.S. 1969. Survival of fish in 164 herbicides, insecticides, fungicides, wetting agents and miscellaneous substances. Int. Pest Control 11(2): 29-35.

Aldridge, W.N. 1976. The influence of organotin compounds on mitochondrial functions. Adv. Chem. Ser. 157: 186-196.

Aldridge, W.N. 1978. The biological properties of organogermanium, -tin and -lead compounds. *In* Plenary lectures 2nd Int. Conf. Organomet. Coord. Chem. Germanium Tin Lead, 1977. *Edited by* M. Gielen and P.G. Harrison. Tel Aviv - Jaffa, Israel. pp. 9-30.

Aldridge, W.N. and Cremer, J.E. 1957. Organotin dithizone complexes. The colorimetric determination of diethyltin and triethyltin compounds. Analyst (London) 82: 37-43.

Aldridge, W.N. and Street, B.W. 1970. Oxidative phosphorylation. The specific binding of trimethyltin and triethyltin to rat liver mitochondria. Biochem. J. 118(1): 171-179.

Aldridge, W.N. and Street, B.W. 1971. Oxidative phosphorylation. The relation between the specific binding of trimethyltin and triethyltin to mitochondria and their effects on various mitochondrial functions. Biochem. J. 124(1): 221-234.

Aldridge, W.N. and Street, B.W. 1981. Spectrophotometric and fluorimetric determination of tri- and di-organotin and -organolead compounds using dithizone and 3-hydroxyflavone. Analyst (London) 106(1258): 60-68.

Aldridge, W.N., Street, B.W. and Skilleter, D.N. 1977. Oxidative phosphorylation. Halide-dependent and halide-independent effects of triorganotin and triorganolead compounds on mitochondrial functions. Biochem. J. 168(3): 353-364.

Aldridge, W.N., Street, B.W. and Noltes, J.G. 1981. The action of 5-co-ordinate triorganotin compounds on rat liver mitochondria. Chem.-Biol. Interact. 34(2): 223-232.

Allen, A.J., Quitter, B.M. and Radick, C.M. 1980. The biocidal mechanism of controlled release bis(tri-n-butyltin) oxide in *Biomphalaria glabrata*. *In* Controlled release of bioactive materials (Symp. 6th Int. Meet. Controlled Release Soc., 1979). *Edited by* R.W. Baker. Academic Press, New York. pp. 399-413.

Allen, D.W., Brooks, J.S., Clarkson, R.W., Mellor, M.T.J. and Williamson, A.G. 1979. Mode of action of organotin stabilizers in PVC: A study by Sn-119m Mössbauer spectroscopy. Chem. Ind. (London) 1979(19): 663-664.

Allen, D.W., Nowell, I.W., Brooks, J.S. and Clarkson, R.W. 1981. Mössbauer and single crystal x-ray studies of polymeric dimethylchlorotin acetate. J. Organomet. Chem. 219(1): 29-34.

Alleston, D.L. and Davies, A.G. 1962. The preparation of some organotin(IV) compounds. J. Chem. Soc. 1962: 2050-2054.

Almenningen, A., Haaland, A. and Motzfeldt, T. 1967. On the molecular structure of dicyclopentadienyllead. J. Organomet. Chem. 7: 97.

Alzieu, C., Thibaud, Y., Héral, M. and Boutier, B. 1980. Evaluation des risques dus à l'emploi des peintures antisalissures dans les zones conchylicoles. Rev. Trav. Inst. Pêches Marit. 44(4): 301-348.

Alzieu, C., Héral, M., Thibaud, Y., Dardignac, M.J. and Feuillet, M. 1982. Influence des peintures antisalissures à base d'organostanniques sur la calcification de la coquille de l'huître *Crassostrea gigas*. Rev. Trav. Inst. Pêches Marit. 45(2): 101-116.

Amdurer, M., Adler, D. and Santschi, P.H. 1983. Studies of the chemical forms of trace elements in sea water using radio tracers. *In* Trace metals in sea water (NATO Conf. Ser. 4:9). *Edited by* C.S. Wong, E. Boyle, K.W. Bruland, J.D. Burton and E.D. Goldberg. Plenum Press, N.Y. pp. 537-562.

American Chemical Society. 1983. Principles of environmental analysis. Committee on Environmental Improvement. Anal. Chem. 55: 2210-2218.

Andreae, M.O. 1983. The determination of the chemical species of some of the "hydride elements" (arsenic, antimony, tin and germanium) in sea water: Methodology and results. In Trace metals in sea water (NATO Conf. Ser. 4:9). Edited by C.S. Wong, E. Boyle, K.W. Bruland, J.D. Burton and E.D. Goldberg. Plenum Press, N.Y. pp. 1-19.

Andreae, M.O. and Byrd, J.T. 1984. Determination of tin and methyltin species by hydride generation and detection with graphite-furnace atomic absorption or flame emission spectrometry. Anal. Chim. Acta 156: 147-157.

Andreae, M.O., Byrd, J.T. and Froehlich, P.N., Jr. 1983. Arsenic, antimony, germanium, and tin in the Tejo Estuary, Portugal: Modeling a polluted estuary. Environ. Sci. Technol. 17(12): 731-737.

Andrews, J. 1903. Analyst (London) 28: 306. (Cited by Price 1962.)

Anon. 1979. Plictran miticide. Tech. Inf. Bull., Dow Chem. Co., Midland, Michigan. (Cited by Blunden et al. 1984b.)

Anon. 1982. Tin research. New horizons open. Chem. Br. 18(12): 850.

Arakawa, Y., Wada, O., Yu, T.H. and Iwai, H. 1981a. Simultaneous determination of trialkyltin homologues in biological materials. J. Chromatogr. 216: 209-217.

Arakawa, Y., Wada, O., Yu, T.H. and Iwai, H. 1981b. Rapid method for the determination of tetraalkyltin compounds in various kinds of biological material by gas chromatography. J. Chromatogr. 207(2): 237-244.

Arakawa, Y., Wada, O. and Manabe, M. 1983. Extraction and fluorometric determination of organotin compounds with Morin. Anal. Chem. 55(12): 1901-1904.

Argaman, Y., Hucks, C.E. and Shelby, S.E., Jr. 1984. The effects of organotin on the activated sludge process. Water Res. 18(5): 535-542.

Ascher, K.R.S. 1979. Fifteen years (1963-1978) of organotin antifeedants - a chronological bibliography. Phytoparasitica 7(2): 117-137.

Ascher, K.R.S. and Nissim, S. 1964. Organotin compounds and their potential use in insect control. World Rev. Pest Control 3(4): 188-211.

Aue, W.A. and Flinn, C.G. 1977. A photometric tin detector for gas chromatography. J. Chromatogr. 142: 145-154.

Aue, W.A. and Flinn, C.G. 1980. Modification of a conventional flame photometric detector for increased tin response. Anal. Chem. 52(9): 1537-1538.

Aue, W.A. and Hastings, C.R. 1973. Response of a filterless flame photometric detector to hetero-organics. J. Chromatogr. 87(1): 232-235.

Aue, W.A. and Hill, H.H., Jr. 1972a. A tin-sensitive hydrogen flame detector. J. Chromatogr. 70(1): 158-161.

Aue, W.A. and Hill, H.H., Jr. 1972b. A hydrogen-rich flame ionization detector sensitive to metals. J. Chromatogr. 74(2): 319-324.

Aue, W.A. and Hill, H.H., Jr. 1973. Selective determination of hetero-organics by a dual-channel detector based on flame conductivity and emission. Anal. Chem. 45: 729-732.

Barnes, J.M. and Stoner, H.B. 1959. The toxicology of tin compounds. Pharmacol. Rev. 11: 211-231.

Barnes, R.D., Bull, A.T. and Poller, R.C. 1973. Studies on the persistence of the organotin fungicide fentin acetate (triphenyltin acetate) in the soil and on surfaces exposed to light. Pestic. Sci. 4(3): 305-317.

Barug, D. 1981. Microbial degradation of bis(tributyltin) oxide. Chemosphere 10(10): 1145-1154.

Barug, D. and Vonk, J.W. 1980. Studies on the degradation of bis(tributyltin) oxide in soil. Pestic. Sci. 11(1): 77-82.

Battais, A., Bensimon, Y., Besson, J., Durand, G. and Pietrasanta, Y. 1982. Etude par polarographie impulsionnelle de la lixiviation en milieu aqueux de peintures contenant des composés organostanniques. Analusis 10(9): 426-432.

Beiter, C.B. 1976. Factors influencing the release of organotin antifoulants from ship bottom paints. In Proc. Int. Controlled Release Pestic. Symp., Akron, Ohio, Sept. 13-15, 1976. pp. 2.22-2.47.

Bennett, R.F. 1983. Industrial development of organotin chemicals. Ind. Chem. Bull. 2(6): 171-176.

Bennett, R.F. and Zedler, R.J. 1966. Biologically active organotin compounds in paint manufacture. J. Oil Colour Chem. Assoc. 49: 928-953.

Berrios-Duran, L.A., Ritchie, L.S. and Wessel, H.B. 1968. Field screening tests on molluscicides against *Biomphalaria glabrata* in flowing water. Bull. W.H.O. 39(2): 316-320.

Black, W.A.P. and Mitchell, R.L. 1952. Trace elements in the common brown algae and in sea water. J. Mar. Biol. Assoc. U.K. 30: 575-584.

Blair, E.H. 1975. Biodegradation of tricyclohexyltin hydroxide. Environ. Qual. Saf. Suppl. 3: 406-409.

Blair, W.R. 1984. Personal communication. National Bureau of Standards, Washington, D.C., 20234.

Blair, W.R., Jackson, J.A., Olsen, G.J., Brinckman, F.E., and Iverson, W.P. 1981. Biotransformation of tin. *In* Proc. 3rd Int. Conf. Heavy Metals in the Environment, Amsterdam, The Netherlands, Sept. 14-18, 1981. CEP Consultants Ltd., Edinburgh. pp. 235-242.

Blair, W.R., Olson, G.J., Brinckman, F.E. and Iverson, W.P. 1982. Accumulation and fate of tri-n-butyltin cation in estuarine bacteria. Microbiol. Ecol. 8(3): 241-251.

Bloodworth, A.J. 1972. Tin and lead. *In* MTP Int. Rev. Sci.: Inorg. Chem., Ser. 1, Vol. 4. *Edited by* B.J. Aylett. Butterworths, London. pp. 275-354.

Blum, J.E. and Bartha, R. 1980. Effect of salinity on methylation of mercury. Bull. Environ. Contam. Toxicol. 25(3): 404-408.

Blum, M.S. and Pratt, J.J., Jr. 1960. Relationships between structure and insecticidal activity of some organotin compounds. J. Econ. Entomol. 53: 445-448.

Blunden, S.J. 1983. The ultraviolet degradation of the methyltin chlorides in carbon tetrachloride and water. J. Organomet. Chem. 248(2): 149-160.

Blunden, S.J. and Chapman, A.H. 1978. Fluorimetric determination of triphenyltin compounds in water. Analyst (London) 103(1233): 1266-1269.

Blunden, S.J. and Chapman, A.H. 1982. The environmental degradation of organotin compounds - a review. Environ. Technol. Lett. 3(6): 267-272.

Blunden, S.J., Smith, P.J. and Sugavanam, B. 1984a. Structure-activity relationships in triorganotin biocides: the influence of the anionic radical. Pestic. Sci. 15: 253-257.

Blunden, S.J., Hobbs, L.A. and Smith, P.J. 1984b. The environmental chemistry of organotin compounds. In Environmental chemistry. Edited by H.J.M. Bowen. The Royal Society of Chemistry, London. pp. 49-77.

Bock, R. 1981. Triphenyltin compounds and their degradation products. Residue Rev. 79: 1-270.

Boettner, E.A., Ball, G.L., Hollingsworth, Z. and Aquino, R. 1981. Organic and organotin compounds leached from PVC and CPVC pipe. Rep. No. EPA-600/1-81-062, Health Effects Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio. 102 pp.

Bokranz, A. and Plum, H. 1975. Industrial manufacture and use of organotin compounds. (Revision of: Fortschritte der chemischen Forschung "Topics in Current Chemistry 16(3/4): 365-403." Springer Verlag, Berlin 1971.) Shering AG. 33 pp.

Booth, M.D. and Fleet, B. 1970. Electrochemical behavior of triphenyltin compounds and their determination at submicrogram levels by anodic stripping voltammetry. Anal. Chem. 42(8): 825- 831.

Boue, S., Gielen, M., Nasielski, J., Austin, J. and Limbourg, M. 1968. On reported selectivity of bromination of mixed tetraalkyltins in carbon tetrachloride. J. Organomet. Chem. 15: 267-268.

Boulton, A.P., Huggins, A.K. and Munday, K.A. 1971. The effects of organometallic antifouling agents on the metabolism of the barnacle Elminius modestus. Toxicol. Appl. Pharmacol. 20(4): 487-501.

Bowen, H.J.M. 1972. The determination of tin in biological material by using neutron-activation analysis. Analyst (London) 97(1161): 1003-1005.

Braman, R.S. and Tompkins, M.A. 1979. Separation and determination of nanogram amounts of inorganic tin and methyltin compounds in the environment. Anal. Chem. 51(1): 12-19.

Breakell, K.R., Morton, T. and Mori, B. 1982. Determination of organotin pesticide residues in crop extracts by gas and liquid chromatography. In Proc. 17th Annu. Workshop for Pesticide Residue Analysts (Western Canada), April 27-29, Vancouver. (Copies available from B. Mori, Health Detection Branch, 601 Customs Building, 1001 West Pender Street, Vancouver, British Columbia V6E 2M7.)

Breitschaft, S. and Basolo, F. 1966. Carbon monoxide exchange with some metal-metal bonded metal carbonyls. J. Am. Chem. Soc. 88(12): 2702-2706.

Brinckman, F.E. 1981. Environmental organotin chemistry today: experiences in the field and laboratory. J. Organomet. Chem. Libr. 12: 343-376.

Brinckman, F.E. and Bellama, J.M. (Editors.) 1978. Organometals and organometalloids, occurrence and fate in the environment. Am. Chem. Soc. Symp. Ser. 82. 447 pp.

Brinckman, F.E. and Iverson, W.P. 1975. Chemical and bacterial cycling of heavy metals in the estuarine system. In Marine chemistry in the coastal environment. Edited by T.M. Church. Am. Chem. Soc. Symp. Ser. 18: 314-342.

Brinckman, F.E., Blair, W.R., Jewett, K.L. and Iverson, W.P. 1977. Application of a liquid chromatograph coupled with a flameless atomic absorption detector for speciation of trace organometallic compounds. J. Chromatogr. Sci. 15(11): 493-503.

Brinckman, F.E., Jackson, J.A., Blair, W.R., Olson, G.J. and Iverson, W.P. 1983. Ultratrace speciation and biogenesis of methyltin transport species in estuarine waters. In Trace metals in sea water (NATO Conf. Ser. 4:9). Edited by C.S. Wong, E. Boyle, K.W. Bruland, J.D. Burton and E.D. Goldberg. Plenum Press, N.Y. pp. 39-72.

Brown, J.M., Chapman, A.C., Harper, R., Mowthorpe, D.J., Davies, A.G. and Smith, P.J. 1972. The characterization of triorganotin hydroxides and of bis(triorganotin) oxides by infrared and Mössbauer spectroscopy. J. Chem. Soc. Dalton Trans. 1972(3): 338-341.

Brownlee, G.S., Walker, A., Nyburg, S.C. and Szymanski, J.T. 1971. Crystal and molecular structure of methyltin trinitrate. J. Chem. Soc. D. 1971(18): 1073.

Bulten, E.J., Gruter, H.F.M. and Martens, H.F. 1976. Synthesis and reactivity of ω-haloalkyltin compounds. J. Organomet. Chem. 117(4): 329-338.

Burns, D.T., Glockling, F. and Harriott, M. 1980. Comparative assessment of gas-liquid chromatography and high-performance liquid chromatography for the separation of tin tetraalkyls and alkyltin halides. J. Chromatogr. 200: 305-308.

Burns, D.T., Glockling, F. and Harriott, M. 1981. Investigation of the determination of tin tetraalkyls and alkyltin chlorides by atomic absorption spectrometry after separation by gas-liquid or high-performance liquid-liquid chromatography. Analyst (London) 106(1266): 921-930.

Buzinova, N.S. 1977. Dynamics of activity of digestive enzymes in fish under the influence of pollutants. J. Ichthyol. (Engl. transl.) 17(5): 805-808.

Buzinova, N.S. and Danil'chenko, O.P. 1984. Reaction of the mollusk *Limnaea stagnalis* L. to pollution. Part II. Physiological and biochemical changes. Biol. Nauki (Moscow) 1: 55-61. (In Russian.)

Byington, K.H., Yeh, R.Y. and Forte, L.R. 1974. The hemolytic activity of some trialkyltin and triphenyltin compounds. Toxicol. Appl. Pharmacol. 27(2): 230-240.

Byrd, J.T. and Andreae, M.O. 1982. Tin and methyltin species in sea-water: concentrations and fluxes. Science 218 (4572): 565-569.

Byrne, A.R. 1974. Neutron activation analysis of tin in biological materials and their ash using ^{123}Sn and ^{125}Sn. J. Radioanal. Chem. 20(2): 627-637.

Cain, K. and Griffiths, D.E. 1977. Studies of energy-linked reactions. Localization of the site of action of trialkyltin in yeast mitochondria. Biochem. J. 162(3): 575-580.

Cain, K., Hyams, R.L. and Griffiths, D.E. 1977. Studies on energy-linked reactions: inhibition of oxidative phosphorylation and energy-linked reactions by dibutyltin dichloride. FEBS Lett. 82(1): 23-28.

Callow, M.E., Millner, P.A. and Evans, L.V. 1979. Organotin resistance in green seaweeds. *In* Proc. 9th Int. Seaweed Symp., 1978. *Edited by* A. Jensen and J.R. Stein. Science Press, Princeton, N.J. pp. 191-197.

Camey, T. and Paulini, E. 1964. Molluscicidal activity of some organotin compounds. Rev. Bras. Malariol. Doencas Trop. 16(4): 487-491. (In Portuguese.)

Cardarelli, N.F. 1974. Slow release molluscicides and related materials. *In* Molluscicides in schistosomiasis control. Proc. Int. Symp., London, England, Oct. 11-12, 1973. *Edited by* T.C. Cheng. Academic Press, New York. pp. 177-240.

Cardarelli, N.F. 1977. Controlled release molluscicides. University of Akron, Akron, Ohio. 36 pp.

Cardarelli, N.F. 1978. Controlled release organotins as mosquito larvicides. Mosq. News 38(3): 328-333.

Cardarelli, N.F. and Evans, W. 1980. Chemodynamics and environmental toxicology of controlled release organotin molluscicides. In Controlled release of bioactive materials (6th Int. Meet. Controlled Release Society, 1979). Edited by N.F. Cardarelli, W. Evans and R.W. Baker. Academic Press, New York. pp. 357-385.

Cardarelli, N.F. et al. 1969. A method of destroying snail vectors of schistosomiasis. Final report (Univ. of Akron, Ohio), World Health Organization, Nov. 10. (Cited by Allen et al. 1980.)

Cardarelli, N.F., Kanakkanatt, S.V., Sherman, L.S. and Cardarelli, B.M. 1983. Organotins as prophylactic agents against cancer: mouse and human studies. Abstract I-2, Proc. 4th Int. Conf. Organometallic and Coordination Chemistry of Germanium, Tin and Lead, August 8-11, Montreal, Quebec.

Cardin, D.J., Keppie, S.A. and Lappert, M.F. 1968. Metal-metal bonds between elements of Group VIA and Group IVB. Inorg. Nucl. Chem. Lett. 4(6): 65-369.

Carraher, C.E., Jr., Giron, D.J., Woelk, W.K., Schroeder, J.A. and Feddersen, M.F. 1979. Characterization of polyethyleneimine modified with organotin halides. Thermal, solubility and fungal properties. J. Appl. Polym. Sci. 23(5): 1501-1508.

Casida, J.E., Kimmel, E.C., Holm, B. and Widmark, G. 1971. Oxidative dealkylation of tetra-, tri-, and dialkyltins and tetra- and trialkylleads by liver microsomes. Acta Chem. Scand. 25(4): 1497-1499.

Cenci, P. and Cremonini, B. 1969. Thin layer chromatography of two organotin pesticides and their behaviour in various soils. Ind. Sacc. Ital. 62(3): 313-316. (In Italian.)

Chapman, A.H. and Price, J.W. 1972. Degradation of triphenyltin acetate by ultra-violet light. Int. Pest Control 14(1): 11-12.

Charlot, G. 1954. Qualitative inorganic chemistry. John Wiley & Sons, New York. 354 pp.

Chau, Y.K. 1983. Personal communication. National Water Research Institute, Burlington, Ontario.

Chau, Y.K. and Wong, P.T.S. 1981. Some environmental aspects of organo-arsenic, lead and tin. In Environmental speciation and monitoring needs for trace metal-containing substances from energy-related processes. Edited by F.E. Brinckman and R.H. Fish. Natl. Bur. Stand. (U.S.) Spec. Publ. 618: 65-80.

Chau, Y.K., Wong, P.T.S., Kramar, O. and Bengert, G.A. 1981. Methylation of tin in the aquatic environment. In Proc. 3rd Int. Conf. Heavy Metals in the Environment. Amsterdam, The Netherlands, Sept. 14-18, 1981. CEP Consultants Ltd., Edinburgh. pp. 641-644.

Chau, Y.K., Wong, P.T.S. and Bengert, G.A. 1982. Determination of methyltin(IV) and tin(IV) species in water by gas chromatography/atomic absorption spectrophotometry. Anal. Chem. 54(2): 246-249.

Chau, Y.K., Maguire, R.J., Wong, P.T.S., Glen, B.A., Bengert, G.A. and Tkacz, R.J. 1984. Occurrence of methyltin and butyltin species in environmental samples in Ontario. Natl. Water Res. Inst. Rep. No. 84-01, National Water Research Institute, Canada Centre for Inland Waters, Environment Canada, Burlington, Ontario. 26 pp.

Chliamovitch, Y.-P. and Kuhn, C. 1977. Behavioural, haematological and histological studies on acute toxicity of bis(tri-n-butyltin) oxide on Salmo gairdneri Richardson and Tilapia rendalli Boulenger. J. Fish Biol. 10(6): 575-585.

Chu, R.C., Barron, G.P. and Baumgarner, P.A.W. 1972. Arsenic determination at sub-microgram levels by arsine evolution and flameless atomic absorption spectrophotometric technique. Anal. Chem. 44(8): 1476-1479.

Cleare, M.J. 1974. Transition metal complexes in cancer chemotherapy. Coord. Chem. Rev. 12(4): 349-405.

Coates, G.E., Green, M.L.H. and Wade, K. 1967. Organometallic compounds. Vol. I. The main group elements. 3rd ed. Methuen and Co., Ltd., London. pp. 413-482.

Cooney, J.J., Hallas, L.E. and Means, J.C. 1981. Tin and microbes in the Chesapeake Bay, U.S.A. In Proc. 3rd Int. Conf. Heavy Metals in the Environment, Amsterdam, The Netherlands, Sept. 14-18, 1981. CEP Consultants Ltd., Edinburgh. pp. 243-245.

Corbin, H.B. 1970. Separation and determination of trace amounts of tin present as organotin residues on fruits. J. Assoc. Off. Anal. Chem. 53(1): 140-146.

Cotton, F.A. and Wilkinson, G. 1962. Advanced inorganic chemistry - a comprehensive text. Interscience Publ., New York. 959 pp.

Cotton, F.A. and Wilkinson, G. 1972. Advanced inorganic chemistry - a comprehensive text. 3rd ed. Interscience Publ., New York. 1145 pp.

Craig, P.J. 1980. The feasibility of environmental methylation for tin - an assessment. Environ. Technol. Lett. 1(5): 225-234.

Craig, P.J. and Rapsomanikis, S. 1981. Biogeochemical cycles of metals and metalloids - the role of methyl-cobalamin and some other chemical routes to methylation in the environment. *In* Environmental speciation and monitoring needs for trace metal-containing substances from energy-related processes. *Edited by* F.E. Brinckman and R.H. Fish. Natl. Bur. Stand. (U.S.) Spec. Publ. 618: 54-64.

Craig, P.J. and Rapsomanikis, S. 1983. Dismutation of trimethyltin species bound to oxo-ligand complexes. Inorg. Chim. Acta 80(3): L19-L21.

Crompton, T.R. 1974. The analysis of organic materials. 4. Chemical analysis of organometallic compounds. Vol. 3. Chap. 9. Academic Press, New York.

Crowe, A.J., Smith, P.J. and Atassi, G. 1980. Investigations into the antitumor activity of organotin compounds. 1. Diorganotin dihalide and di-pseudohalide complexes. Chem.-Biol. Interact. 32(1-2): 171-178.

Crowe, A.J., Smith, P.J., Cardin, C.J., Parge, H.E. and Smith, F.E. 1984. Possible pre-dissociation of diorganotin dihalide complexes: relationship between antitumor activity and structure. Cancer Lett. 24: 45-48.

Da Costa, E.W.B. and Osborne, L.D. 1972. Laboratory evaluations of wood preservatives. 7. Effect of chemical structure on toxicity of organotin and organolead compounds to wood-destroying fungi. Holzforschung 26(3): 114-118.

Danil'chenko, O.P. 1977. The sensitivity of fish embryos to the effect of toxicants. J. Ichthyol. (Engl. transl.) 17: 455-463.

Danil'chenko, O.P. and Stroganov, N.S. 1975. Evaluation of the effects of toxic substances in water on the ontogenesis of fish. Vopr. Ikthiol. 15(12): 346-355. (In Russian.)

Davies, A.G. and Smith, P.J. 1980. Recent advances in organotin chemistry. Adv. Inorg. Chem. Radiochem. 23: 1-77.

Davies, A.G. and Smith, P.J. 1982. Tin. In Comprehensive organometallic chemistry: The synthesis, reactions and structures of organometallic compounds. Vol. 2. Edited by G. Wilkinson, F.G.A. Stone and E.W. Abel. Pergamon Press, N.Y. pp. 519-627.

Davies, A.G., Kleinschmidt, D.C., Palan, P.R. and Vasishtha, S.C. 1971. Organotin chemistry. 11. The preparation of organotin alkoxides. J. Chem. Soc. C. 1971(23): 3972-3976.

Davies, A.G., Smith, L. and Smith, P.J. 1972. Organotin chemistry. 12. The structure and reactions of some mono-organotin(IV) compounds. J. Organomet. Chem. 39(2): 279-288.

Dawans, F. 1982. Les peintures marines antisalissures à base de polymères organostanniques. Rev. Inst. Fr. Pet. 37(6): 767-807.

de la Court, F.H. 1977. Fouling resistant coatings: Their functioning and future developments. Proc. Int. Conf. Org. Coat. Sci. Technol. Vol. 3. pp. 97-137.

de la Court, F.H. and de Vries, H.J. 1977. The leaching mechanism of some organotin-toxicants from anti-fouling paints. C.R. 4^{e} Congr. Int. Corrosion Mar. Salissures, Antibes-Juan-les-Pins, France, June 14-18, 1976. pp. 113-118.

Desaiah, D., Cutkomp, L.K. and Koch, R.B. 1973. Inhibition of spider mite ATPases by Plictran and three organochlorine acaricides. Life Sci. 13(12): 1693-1703.

Deschiens, R. and Floch, H. 1962. Les propriétés molluscicides du chlorure et de l'acétate de triphénylétain dans le cadre de la prophylaxie des bilharzioses. C.R. Acad. Sci. Paris 255: 1236-1237.

Deschiens, R. and Floch, H.A. 1968. Action biologique comparée de 6 molluscicides chimiques dans le cadre de la prophylaxie des bilharzioses. Conclusions pratiques. Bull. Soc. Pathol. Exot. 61(4): 640-650.

Deschiens, R., Brottes, H. and Mvogo, L. 1966. Application sur le terrain, au Caméroun, dans la prophylaxie des bilharzioses de l'action molluscicide de l'oxyde de tributylétain. Bull. Soc. Pathol. Exot. 59(2): 968-973.

de Villiers, J.P. 1965. The development of molluscicides. S. Afr. Ind. Chem. 19(10-12): 166-170.

de Villiers, J.P. and MacKenzie, J.G. 1963. Organotin and organolead molluscicides. WHO unpublished document Mol/Inf/13. VIII/63. (Cited by Duncan 1980.)

Dizikes, L.J., Ridley, W.P. and Wood, J.M. 1978. A mechanism for the biomethylation of tin by reductive Co-C bond cleavage of alkylcobalamins. J. Am. Chem. Soc. 100(3): 1010-1012.

Dogan, S. and Haerdi, W. 1980. Determination of total tin in environmental biological and water samples by atomic absorption spectrometry with graphite furnace. Int. J. Environ. Anal. Chem. 8(4): 249-257.

Dressler, M., Martineau, V. and Janak, J. 1971. Response of the alkali flame ionisation detector to silicon, tin and lead compounds. J. Chromatogr. 59(2): 429-433.

Duncan, J. 1980. The toxicology of molluscicides. The organotins. Pharmacol. Ther. 10(2): 407-429.

Dyer, R.S., Walsh, T.J., Swartzwelder, H.S. and Wayner, M.J. 1982. Neurotoxicology of the alkyltins. Neurobehav. Toxicol. Teratol. 4(2): 1-278.

Elliott, B.M., Aldridge, W.N. and Bridges, J.W. 1979. Triethyltin binding to cat haemoglobin. Evidence for two chemically distinct sites and a role for both histidine and cysteine residues. Biochem. J. 177(2): 461-470.

Environment Canada and Health and Welfare Canada. 1979. Environmental Contaminants Act. Priority Chemicals - 1979. In The Canada Gazette, Part 1, Dec. 1. pp. 7365-7370.

Esposto, R., Camoni, I., Chiacchierini, E. and Magri, A. 1978. Determination of triphenyltin compounds and tricyclohexyltin hydroxide by gas chromatography of their derivatives. Ann. Chim. (Rome) 68(3-4): 235-245.

Estes, S.A., Poirier, C.A., Uden, P.C. and Barnes, R.M. 1980. Gas chromatography with plasma emission spectroscopic detection of Friedel-Crafts catalyzed alkyl group redistribution products among Si, Ge, Sn and Pb atoms. J. Chromatogr. 196(2): 265-277.

Estes, S.A., Uden, P.C. and Barnes, R.M. 1982. Plasma emission spectral detection for high-resolution gas chromatographic study of Group IV organometallic compounds. J. Chromatogr. 239: 181-189.

Evans, C.J. 1974. Developments in the organotin industry. 2. Di-organotin compounds. Tin Its Uses 101: 12-15.

Evans, C.J. and Smith, P.J. 1975. Organotin-based antifouling systems. J. Oil Colour Chem. Assoc. 58(5): 160-168.

Evans, D.W. and Laughlin, R.B., Jr. 1984. Accumulation of bis(tributyltin) oxide by the mud crab, *Rhithropanopeus harrisii*. Chemosphere 13(1): 213-219.

Evans, L.V. 1981. Marine algae and fouling: A review, with particular reference to ship-fouling. Bot. Mar. 24(4): 167-171.

Fanchiang, Y.-T. and Wood, J.M. 1981. Alkylation of tin by alkylcobalamins. Kinetics and mechanism. J. Am. Chem. Soc. 103(17): 5100-5103.

Fanchiang, Y.-T., Ridley, W.P. and Wood, J.M. 1978. Kinetic and mechanistic studies on B_{12}-dependent methyl transfer to certain toxic metal ions. *In* Organometals and organometalloids. Occurrence and fate in the environment. *Edited by* F.E. Brinckman and J.M. Bellama. Am. Chem. Soc. Symp. Ser. 82: 54-64.

FAO. 1969. FAO Fish. Tech. Pap. No. 94, FAO, Rome. 110 pp. (Cited by Jensen 1977.)

Farnsworth, M. and Pekola, J. 1961. Tin. *In* Treatise on analytical chemistry. Part 2. Vol. 3. *Edited by* I.M. Kolthoff, P.J. Elving and E.B. Sandell. Interscience Publ., New York. p. 351.

Figge, K., Koch, J. and Lubba, H. 1977. Contribution to the gas chromatographic analysis of organotin stabilizers for polyvinyl chloride. J. Chromatogr. 131: 317-327. (In German.)

Filenko, O.F. and Isakova, E.F. 1979. Dynamics of the accumulation of triphenyltin chloride by *Daphnia*. Biol. Nauki (Moscow) 0(3): 46-49. (In Russian.)

Filenko, O.F. and Parina, O.V. 1981. Quantitative interrelationship of the accumulation of organotin compounds and inorganic phosphate by carp tissues. Vestn. Mosk. Univ. Biol. 36(3): 46-52.

Filenko, O.F. and Parina, O.V. 1982. Distribution of trialkyltin chlorides in organs as a factor determining their toxicity for the carp. Biol. Nauki (Moscow) 0(4): 54-57. (In Russian.)

Filenko, O.F. and Parina, O.V. 1983. Organotin compounds and the regulation of phosphate intake in organs and tissues of carp. *In* Reakts. Gidrobiontov Zagryaz. *Edited by* N.S. Stroganov. Izd. Nauka, Moscow. pp. 151-158. (In Russian.)

Fischer, E.C. 1976. Increasing economic importance of marine fouling control. *In* Proc. Int. Controlled Release Pestic. Symp., Akron, Ohio, Sept. 13-15, 1976. pp. 2.1-2.3.

Fleet, B. and Fouzder, N.B. 1975. Electrochemical behaviour of organotin compounds. Part I. Application to the determination of trialkyl- and triaryltin derivatives. J. Electroanal. Chem. Interfacial Electrochem. 63(1): 59-68.

Floch, H. and Deschiens, R. 1962. Étude comparée de l'action molluscicide du 5,2'-dichloro-4'-nitro-salicylanilide (Bayer 73) et des sels (acêtate et chlorure) de triphényl-étain. Bull. Soc. Pathol. Exot. 55: 816-831.

Floch, H., Deschiens, R. and Floch, T. 1964. Sur le propriétés molluscicides de l'oxyde et de l'acêtate de tributyl-étain (prophylaxie des bilharzioses). Bull. Soc. Pathol. Exot. 57(3): 454-465.

Ford, B.F.E., Liengme, B.V. and Sams, J.R. 1969. Organotin carboxylates. 1. Mössbauer and infrared study of triphenyltin carboxylates and novel compounds RSn(O)OCOR. J. Organomet. Chem. 19(1): 53-65.

Frankland, E. 1849. Ann. Chem. 71: 171.

Freitag, K.-D. and Bock, R. 1974a. Analysis of mixtures containing tri-, di- and monophenyltin compounds and inorganic tin(IV). Fresenius Z. Anal. Chem. 270(5): 337-346. (In German.)

Freitag, K.-D. and Bock, R. 1974b. Degradation of triphenyltin chloride on sugar beet plants and in rats. Pestic. Sci. 5(6): 731-739.

Frick, L.P. and de Jimenez, W.Q. 1964. Molluscicidal qualities of three organo-tin compounds revealed by 6-hour and 24-hour exposures against representative stages and sizes of Australorbis glabratus. Bull. W.H.O. 31(3): 429-431.

Furr, A.K., Lawrence, A.W., Tong, S.S.C., Grandolfo, M.C., Hofstader, R.A., Bache, C.A., Gutenmann, W.H. and Lisk, D.J. 1976. Multielement and chlorinated hydrocarbon analysis of municipal sewage sludges of American cities. Environ. Sci. Technol. 10(7): 683-687.

Gardner, B.G. and Poller, R.C. 1964. Insecticidal activity and structure of some organotin compounds. Bull. Entomol. Res. 55(1): 17-21.

Gauer, W.O., Seiber, J.N. and Crosby, D.G. 1974. Determination of organotin residues from Plictran in fruit crops by gas-liquid chromatography. J. Agric. Food Chem. 22(2): 252-254.

Getzendaner, M.E. and Corbin, H.B. 1972. Residues on apples and pears from use of Plictran miticide. J. Agric. Food Chem. 20(4): 881-885.

Gielen, M., Jurkschat, K. and Atassi, G. 1984. Bis(halophenylstannyl) methanes: new organotin compounds exhibiting anti-tumor activity. Bull. Soc. Chim. Belg. 93(2): 153-155.

Gile, J.D., Collins, J.C. and Gillett, J.W. 1982. Fate and impact of wood preservatives in a terrestrial microcosm. J. Agric. Food Chem. 30: 295-301.

Gitlitz, M.H. (Inventor.) 1975. Triorganotin compounds used to combat plant fungi. M & T Chemicals Inc., assignee. U.S. Patent 3,923,998. 1975 December 2. 6 pp.

Gitlitz, M.H. 1976. Organotins in agriculture. Adv. Chem. Ser. 157: 167-176.

Glockling, F. 1980. Organometallic compounds in relation to pollution. Anal. Proc. (London) 17(10): 417-422.

Goldberg, D.E., Harris, D.H., Lappert, M.F. and Thomas, K.M. 1976. A new synthesis of divalent group 4B alkyls $M(CH(SiMe_3)_2)_2$ (M = Ge or Sn), and the crystal and molecular structure of the tin compound. J. Chem. Soc. Chem. Commun. 1976(7): 261-262.

Goldberg, E.D., Hodge, V.F., Griffin, J.J., Koide, M. and Edgington, D.N. 1981. Impact of fossil fuel combustion on the sediments of Lake Michigan. Environ. Sci. Technol. 15(4): 466-471.

Good, M.L., Dundee, D.S. and Swindler, G. 1980. Bioassays and environmental effects of organotin marine antifoulants. *In* Controlled release of bioactive materials (Symp. 6th Int. Meet. Controlled Release Soc., 1979). *Edited by* R.W. Baker. Academic Press, New York. pp. 387-397.

Gould, J.M. 1976. Inhibition by triphenyltin chloride of a tightly-bound membrane component involved in photophosphorylation. Eur. J. Biochem. 62(3): 567-575.

Gras, G. and Rioux, J.-A. 1965. Relation entre la structure chimique et l'activité insecticide des composés organiques de l'étain (essai sur les larves de *Culex pipiens pipiens* L.). Arch. Inst. Pasteur Tunis 42(1): 9-22.

Great Lakes Water Quality Board. 1976. Organotin compounds. *In* Annual report of the Water Quality Objectives Subcommittee and the Task Force on the Scientific Basis for Water Quality Criteria. pp. 33-44.

Grün, L. and Fricker, H.H. 1963. Organotin compounds as disinfectants. Tin Its Uses 61: 8-10.

Guard, H.E., Cobet, A.B. and Coleman, W.M., III. 1981. Methylation of trimethyltin compounds by estuarine sediments. Science 213(4509): 770-771.

Guard, H.E., Coleman, W.M., III and Cobet, A.B. 1982. Speciation of tributyltin compounds in seawater and estuarine sediments. Presented to Div. Environ. Chem., Am. Chem. Soc., March, Las Vegas, Nevada.

Gutknecht, W.F., Grohse, P.M., Homzak, C.A., Tronzo, C., Ranade, M.B. and Damle, A. 1982. Development of a method for the sampling and analysis of organotin compounds. U.S. Natl. Inst. Occup. Saf. Health Rep. No. 210-80-0066. 137 pp.

Guyot, A., Michel, A. and Hoang, T.V. 1981. Basic mechanism for tin stabilizers in polyvinylchloride. Org. Coat. Appl. Polym. Sci. Proc. 46: 562-567.

Hallas, L.E. and Cooney, J.J. 1981a. Tin and tin-resistant microorganisms in Chesapeake Bay. Appl. Environ. Microbiol. 41(2): 466-471.

Hallas, L.E. and Cooney, J.J. 1981b. Effects of stannic chloride and organotin compounds on estuarine microorganisms. Dev. Ind. Microbiol. 22: 529-535.

Hallas, L.E., Means, J.C. and Cooney, J.J. 1982a. Methylation of tin by estuarine microorganisms. Science 215(4539): 1505-1507.

Hallas, L.E., Thayer, J.S. and Cooney, J.J. 1982b. Factors affecting the toxic effect of tin on estuarine microorganisms. Appl. Environ. Microbiol. 44(1): 193-197.

Hamaguchi, H., Kuroda, R., Onuma, N., Kawabuchi, K., Mitsubayashi, T. and Hosohara, K. 1964. The geochemistry of tin. Geochim. Cosmochim. Acta 28(7): 1039-1053.

Hammann, I., Buechel, K.H., Bungarz, K. and Born, L. 1978. Peropal, a new acaricide. Pflanzenschutz-Nachr. 31(1): 61-83.

Hansen, D.R., Gilfoil, T.J. and Hill, H.H., Jr. 1981. Comparison of metal-sensitive flame ionization and carbon-sensitive flame ionization detectors for the gas chromatographic determination of organotins. Anal. Chem. 53(6): 857-861.

Harris, L.R., Andrews, C., Burch, D., Hampton, D. and Maegerlein, S. 1979. Soil disposal of organotin-contaminated grit waste. David W. Taylor Naval Ship Research and Development Center, Bethesda, Maryland. Rep. DTNSRDC/SME-78/2A. 55 pp.

Harrison, P.G., King, T.J. and Healy, M.A. 1979. Structural studies in main group chemistry. XXIII. Estertin derivatives. Structural and spectroscopic studies. J. Organomet. Chem. 182(1): 17-36.

Hasebe, K., Yamamoto, Y. and Kambara, T. 1982. Differential pulse polarographic determination of organotin compounds coated on fishing nets. Fresenius Z. Anal. Chem. 310: 234-238.

Hattori, Y., Kuge, Y. and Nakamoto, M. 1984. Determination of tripropyltin chloride in environmental water and sediment. Jpn. Anal. 33(1): E43-E46.

Hausler, D.W. and Taylor, L.T. 1981. Nonaqueous on-line simultaneous determination of metals by size exclusion chromatography with inductively coupled plasma atomic emission spectrometric detection. Anal. Chem. 53(8): 1223-1227.

Havir, J. and Vrestal, J. 1972. Determination of trialkyltin compounds in water. Vodni Hospod. B 22(12): 323-325. (In Czechoslovakian.)

Hayashi, K., Iyoda, J. and Shiihara, I. 1967. Reaction of organotin oxides, alkoxides and acyloxides with organosilicon hydrides. New preparative method of organotin hydrides. J. Organomet. Chem. 10(1): 81-94.

Hayes, W.J., Jr. 1982. Inorganic and organometal pesticides. In Pesticides studied in man. Williams and Wilkins, Baltimore. pp. 35-38.

Hedges, E.S. 1960. The scope of organotin compounds in industry. Research (London) 13: 449-552.

Henderson, A. and Holliday, A.K. 1965. Reactions of tetravinyltin with carboxylic acids. Properties of tin(IV) tetracarboxylates. J. Organomet. Chem. 4(5): 377-381.

Héral, M., Razet, D. and Garnier, J. 1981. Répartition géographique des malformations de la coquille de l'huitre Crassostrea gigas à proximité du port de Boyardville. Rapport I.S.T.P.M. (Inst. Sci. Tech. Pêches Marit.), Novembre 1981. 6 pp. (Cited by Alzieu et al. 1980.)

Hill, R. 1984. Int. Res. Group Wood Preserv., Doc. No. IRG/WP/3312, Stockholm.

His, E. and Robert, R. 1980. Action d'un sel organo-métallique, l'acétate de tributyle-étain sur les oeufs et les larves D de Crassostrea gigas (Thunberg). Cons. Int. Explor. Mer, Comité de la Mariculture 1980/F:27. 10 pp.

His, E. and Robert, R. 1981a. Les causes de mortalités larvaires de *Crassostrea gigas* dans le bassin d'Arcachon. Rapport *I.S.T.P.M.* (Inst. Sci. Tech. Pêches Marit.). 31 pp. + annexes. (Cited by Alzieu *et al*. 1980.)

His, E. and Robert, R. 1981b. Effects of copper chloride on the eggs and D larvae of *Crassostrea gigas* (Thunberg). Preliminary results. Int. Counc. Explor. Sea, Mariculture Committee Rep. CM 1981/F:43.

His, E., Maurer, D. and Robert, R. 1983. Estimation de la teneur en acétate de tributyle-étain dans l'eau de mer, par une méthode biologique. J. Moll. Stud. (Suppl. 12A): 60-68.

Hodge, V.F., Seidel, S.L. and Goldberg, E.D. 1979. Determination of tin(IV) and organotin compounds in natural waters, coastal sediments and macro algae by atomic absorption spectrometry. Anal. Chem. 51(8): 1256-1259.

Hoffman, J.F., Kappel, K.C., Frenzel, L.M. and Good, M.L. 1978. Infrared and nuclear magnetic resonance analysis of organotin toxicants for marine antifouling coatings. *In* Organometallic polymers. *Edited by* C.E. Carraher, Jr., J.E. Sheats and C.U. Pittman, Jr. Academic Press, New York. pp. 195-205.

Hopf, H.S. and Muller, R.L. 1962. Laboratory breeding and testing of *Australorbis glabrata* for molluscicidal screening. Bull. W.H.O. 27: 783-789.

Hopf, H.S., Duncan, J., Beesley, J.S.S., Webley, D.J. and Sturrock, R.F. 1967. Molluscicidal properties of organotin and organolead compounds with particular reference to triphenyllead acetate. Bull. W.H.O. 36(6): 955-961.

Horwitz, W. 1979. Commonly used methods of analysis for tin in foods. J. Assoc. Off. Anal. Chem. 62(6): 1251-1264.

Horn, M.K. and Adams, J.A.S. 1966. Computer-derived geochemical balances and element abundances. Geochim. Cosmochim. Acta 30(3): 279-297.

Houk, C.C. and Beaulieu, H.J. 1981. Sampling and breakthrough studies with Plictran. *In* Chemical hazards in the workplace - measurement and control. *Edited by* G. Choudhary. Am. Chem. Soc. Symp. Ser. 149: 109-121.

Hsu, K.-H. 1982. New marine antifouling coatings containing organotin and chlorophenol compounds as antifouling agents. Diss. Abstr. Int. B 43(6): 1867.

Huey, C., Brinckman, F.E., Grim, S. and Iverson, W.P. 1974. The role of tin in bacterial methylation of mercury. In Proc. Int. Conf. Transport of Persistent Chemicals in Aquatic Ecosystems. Ottawa, Ontario, May 1-3, 1974. Edited by A.S.W. deFreitas, D.J. Kushner, Q.N. LaHam and S.A. Qadri. National Research Council of Canada, Ottawa. pp. II-73 - II-78.

Huheey, J.E. 1978. Inorganic chemistry: Principles of structure and reactivity. 2nd ed. Harper and Row, New York. 889 pp.

Hulme, R. 1963. The crystal and molecular structure of chloro(trimethyl)-pyridinetin(IV). J. Chem. Soc. 1963: 1524-1527.

Hutton, R.E., Burley, J.W. and Oakes, V. 1978. β-substituted alkyltin halides. 1. Monoalkyltin trihalides: synthetic, mechanistic and spectroscopic aspects. J. Organomet. Chem. 156(2): 369-382.

Imura, H. and Suzuki, N. 1983. Fractional separation of organic and inorganic tin compounds and determination by substoichiometric isotope dilution analysis. Anal. Chem. 55(7): 1107-1111.

Ingham, R.K., Rosenberg, S.D. and Gilman, H. 1960. Organotin compounds. Chem. Rev. 60: 459-539.

Ishii, T. 1982. Tin in marine algae. Bull. Jpn. Soc. Sci. Fish. 48(11): 1609-1615.

Ison, R.R., Newbold, G.T. and Saggers, D.T. 1971. Biocidal activities of some heterocyclic organotin sulphides. Pestic. Sci. 2(4): 152-159.

Iverson, W.P. and Brinckman, F.E. 1978. Microbial metabolism of heavy metals. In Water pollution microbiology. Vol. 2. Edited by R. Mitchell. J. Wiley & Sons, New York. pp. 201-232.

Jackson, J.A., Blair, W.R., Brinckman, F.E. and Iverson, W.P. 1982. Gas-chromatographic speciation of methylstannanes in the Chesapeake Bay using purge and trap sampling with a tin-selective detector. Environ. Sci. Technol. 16(2): 110-119.

Jeltes, R. 1969. Determination of bis(tributyltin) oxide in air by atomic absorption spectroscopy or pyrolysis gas chromatography. Ann. Occup. Hyg. 12(4): 203-207.

Jensen, K. 1977. Organotin compounds in the aquatic environment - a survey. Biokon Rep. 4: 1-8.

Jessen, E.B., Taugbol, K. and Griebrokk, T. 1979. Separation and purification of organotin halides. J. Chromatogr. 168(1): 139-142.

Jewett, K.L. and Brinckman, F.E. 1981. Speciation of trace di- and triorganotins in water by ion-exchange HPLC-GFAA. J. Chromatogr. Sci. 19(11): 583-593.

Jin, K., Kanetoshi, A. and Kaneshima, H. 1982. Environmental and biological effects of organotin pesticides: residues of tricyclohexyltin hydroxide in orchard. II. Hokkaidoritsu Eisei Kenkyushoho 32: 71-72. (In Japanese.) (See also Biol. Abstr. 101: 18947c.)

Jitsu, Y., Kudo, N., Sato, K. and Teshima, T. 1969. Determination of organotin compounds by gas-liquid chromatography. Bunseki Kagaku (Jpn. Anal.) 18(2): 169-175. (In Japanese.)

Jolyet, F. and Cahours, A. 1869. Recherches sur l'action physiologique des stannéthyles et des stanméthyles. C.R. Acad. Sci. Paris 68: 1276-1280.

Jonas, R.B. and Cooney, J.J. 1983. Accumulation of inorganic- and organo-tin by tin resistant estuarine microorganisms. Abstr. Annu. Meet. Am. Soc. Microbiol. 83: 227.

Jones, W.R., Jr. 1973. Friction, wear, and thermal stability studies of some organotin and organosilicon compounds. NASA Tech. Note D-7175. 17 pp.

Jones, K. and Lappert, M.F. 1965. Amino derivatives of metals and metalloids. 1. Preparation of aminostannanes, stannylamines, and stannazanes. J. Chem. Soc. 1965: 1944-1951.

Jones, P.A. and Millson, M.F. 1982. Organotins in the Canadian environment: a synopsis. Environmental Protection Service Rep. EPS 3-EC-82-1, Environment Canada.

Kaars Sijpesteijn, A., Rijkens, F., Luijten, J.G.A. and Willemsens, L.C. 1962. On the antifungal and antibacterial activity of some trisubstituted organogermanium, organotin and organolead compounds. Antonie van Leeuwenhoek J. Microbiol. Serol. 28: 346-356.

Kaars Sijpesteijn, A., Luijten, J.G.A. and van der Kerk, G.J.M. 1969. Organometallic fungicides. In Fungicides - An advanced treatise. Vol. II. Edited by D.C. Torgeson. Academic Press, New York and London. pp. 331-366.

Kahana, L. and Kaars Sijpesteijn, A. 1967. Studies on the mode of action of the antibacterial agent diethyltin dichloride on Escherichia coli. Antonie van Leeuwenhock J. Microbiol. Serol. 33: 427-438.

Kahn, J.S. 1968. Chlorotri-*n*-butyltin: an inhibitor of photophosphorylation in isolated chloroplasts. Biochim. Biophys. Acta 153(1): 203-210.

Kandil, S.A. and Allred, A.L. 1970. Tertiary butyl derivatives of tin. J. Chem. Soc. A 1970(18): 2987-2992.

Kapila, S. and Vogt, C.R. 1980. Some aspects of organic tin analysis by gas chromatography - flame photometry. J. Chromatogr. Sci. 18(3): 144-147.

Kenaga, E.E. (Inventor.) 1975. Triaryltin compounds as chemosterilants. U.S.A. Dow Chemical Co., assignee. U.S. patent 3,891,767. 1975 June 24. 10 pp.

Kenis, P. and Zirino, A. 1983. Quantitative measurement of tributyltin oxide in sea water by differential pulse anodic stripping voltammetry. Anal. Chim. Acta 149: 157-166.

Kerr, K.G. 1952. Butynorate, an effective and safe substance for the removal of *Raillietina cesticillus* from chickens. Poult. Sci. 31: 328-336.

Kimmel, E.C., Fish, R.H. and Casida, J.E. 1977. Bioorganotin chemistry. Metabolism of organotin compounds in microsomal monooxygenase systems and in mammals. J. Agric. Food Chem. 25(1): 1-9.

Kleinkopf, M.D. 1960. Spectrographic determination of trace elements in lake waters from Northern Maine. Bull. Geol. Soc. Am. 71: 1231-1242.

Knauf, W. 1974. Brestan 60 - Fischtoxizität; interner Versuchsbericht der Pflanzenschutz - Forschung der HOECHST AG, 24.1. (Cited by Bock 1981.)

Knowles, C.O. 1976. Chemistry and toxicology of quinoxaline, organotin, organofluorine and formamidine acaricides. Environ. Health Perspect. 14: 93-102.

Knox, S.A.R., Mitchell, C.M. and Stone, F.G.A. 1969. Organo-silicon and -tin complexes of osmium carbonyl. J. Organomet. Chem. 16(3): P67-P68.

Kocheshkov, K.A. 1926. A new class of aryltin derivatives. Phenyltrihalostannane. Ber. Dent. Chem. Ges. 62B: 1659.

Kojima, S. 1979. Separation of organotin compounds by using the difference in partition behaviour between hexane and methanolic buffer solution. Part 1. Determination of butyltin compounds in textiles by graphite furnace atomic absorption spectrophotometry. Analyst (London) 104(1240): 660-667.

Komora, F. and Popl, M. 1978. The resistance of bis-tributyltin oxide to oxidation and elevated temperatures. Holztechnologie 19(3): 145-147. (In German.)

Krampitz, G. 1980. Studies on oyster jelly. Personal communication. (Cited by Alzieu _et_ _al_. 1980.)

Kuivila, H.G. and Levins, P.L. 1964. Protonolysis of the tin-hydrogen bond. Kinetics and mechanism. J. Am. Chem. Soc. 86(1): 23-27.

Kumpulainen, J. and Koivistoinen, P. 1977. Advances in tin compound analysis with special reference to organotin pesticide residues. Residue Rev. 66: 1-18.

Kuwahara, R., Suzuki, T. and Meguro, H. 1980. Determination of a fungicide, triphenyltin chloride, in soil by the direct-insertion selected ion monitoring method. Agric. Biol. Chem. 44(3): 669-670.

Lancashire, W.E. and Griffiths, D.E. 1975. Studies on energy-linked reactions: isolation, characterization and genetic analysis of trialkyltin resistant mutants of _Saccharomyces cerevisiae_. Eur. J. Biochem. 51(2): 377-392.

Lantzy, R.J. and Mackenzie, F.T. 1979. Atmospheric trace metals: global cycles and assessment of man's impact. Geochim. Cosmochim. Acta 43(4): 511-525.

Lapp, T.W. 1976. Study on chemical substances from information concerning the manufacture, distribution, use, disposal, alternatives, and magnitude of exposure to the environment and man. Task II - The manufacture and use of selected alkyltin compounds. Environmental Protection Agency, Office of Toxic Substances, EPA 560/6-76-011, PB-251819. 122 pp.

Lappert, M.F. and Jones, K. (Inventors.) 1966. Organotin compounds. Britain patent 1,026,405. 1966 April 20. 4 pp.

Laughlin, R.B., Jr. 1984. Personal communication. University of California, Naval Biosciences Laboratory, Naval Supply Center, Oakland, California 94625.

Laughlin, R.B., Jr. and French, W.J. 1980. Comparative study of the acute toxicity of a homologous series of trialkyltins to larval shore crabs, Hemigrapsus nudus, and lobster, Homarus americanus. Bull. Environ. Contam. Toxicol. 25(5): 802-809.

Laughlin, R. and Lindén, O. 1982. Sublethal responses of the tadpoles of the European frog Rana temporaria to two tributyltin compounds. Bull. Environ. Contam. Toxicol. 28(4): 494-499.

Laughlin, R., Lindén, O. and Guard, H. 1982. Toxicity of tributyltins and leachates from antifouling paints on marine amphipods. Inst. Vatten. Luftvaardsforsk., IVL Publ. B 676. 20 pp.

Laughlin, R.B., Jr., French, W., Johannesen, R.B., Guard, H.E. and Brinckman, F.E. 1984a. Predicting toxicity using computed molecular topologies: the example of triorganotin compounds. Chemosphere 13(4): 575-584.

Laughlin, R., Nordlund, K. and Lindén, O. 1984b. Long-term effects of tributyltin compounds on the Baltic amphipod, Gammarus oceanicus. Mar. Environ. Res. 12: 243-271.

Lecomte, C., Protas, J. and Devaud, M. 1976. Dichlorohydroxo(ethyl)tin ($C_2H_5SnOHCl_2.H_2O$). Acta Crystallogr. B32: 923-924.

Leeuwangh, P., Nijman, W., Visser, H., Kolar, Z. and de Goey, J.J.M. 1976. Toxicity of triphenyltin fungicides in the aquatic environment. Meded. Fac. Landbouwwet. Rijksuniv. Gent 41/2: 1483-1490.

Lindén, E., Bengtsson, B.-E., Svanberg, O. and Sundström, G. 1979. The acute toxicity of 78 chemicals and pesticide formulations against two brackish water organisms, the bleak (Alburnus alburnus) and the harpacticoid Nitocra spinipes. Chemosphere 8(11/12): 843-851.

Lindner, E., Kunze, U., Ritter, G. and Haag, A. 1970. Behavior of tetraorganotin compounds with liquid sulfur dioxide. J. Organomet. Chem. 24(1): 119-129. (In German, with English abstract.)

Litan, R., Basters, J., Martijn, A., van der Molen, T., Pasma, P., Rabenort, B. and Smink, J. 1978. Potentiometric method for determining triphenyltin compounds in formulations: collaborative study. J. Assoc. Off. Anal. Chem. 61(6): 1504-1506.

Lloyd, D. and Edwards, S.W. 1977. Mitochondrial adenosine triphosphatase of the fission yeast Schizosaccharomyces pombe 972h$^-$. Changes in inhibitor sensitivities during the cell cycle indicate similarities and differences in binding sites. Biochem. J. 162: 581-590.

Lu, X.-K. and Thompson, J.A.J. 1983. Unpublished data. Institute of Ocean Sciences, Sidney, British Columbia.

Luijten, J.G.A. 1972. Applications and biological effects of organotin compounds. In Organotin compounds. Vol. 3. Edited by A.K. Sawyer. Marcel Dekker, New York. pp. 931-974.

Luijten, J.G.A. and Klimmer, O.R. 1975. A toxicological assessment of organotin compounds. Int. Tin Res. Inst. Publ. 501D. (English translation found in Appendix D, Smith 1978.)

Luijten, J.G.A. and van der Kerk, G.J.M. 1961. Investigations on organo-tin compounds. XIV. Preparation and antifungal properties of some triaryl- and triarylalkyl-tin acetates. J. Appl. Chem. 11(1): 35-37.

M & T. 1979. Speciation of butyltins in fish tissues by solvent separation and aas-graphite furnace. Standard Test Method AA-33, M & T Chem. Inc., Rahway, New Jersey. 7 pp.

Macchi, G. and Pettine, M. 1980. Voltammetric characterization and chemical behavior of inorganic tin in natural waters. Environ. Sci. Technol. 14(7): 815-818.

MacCrehan, W.A. 1981. Differential pulse detection in liquid chromatography and its application to the measurement of organometal cations. Anal. Chem. 53(1): 74-77.

Maguire, R.J. 1984. Butyltin compounds and inorganic tin in sediments in Ontario. Environ. Sci. Technol. 18(4): 291-294.

Maguire, R.J. and Huneault, H. 1981. Determination of butyltin species in water by gas chromatography with flame photometric detection. J. Chromatogr. 209(3): 458-462.

Maguire, R.J. and Tkacz, R.J. 1983. Analysis of butyltin compounds by gas chromatography: comparison of flame photometric and atomic absorption spectrophotometric detectors. J. Chromatogr. 268(1): 99-101.

Maguire, R.J., Chau, Y.K., Bengert, G.A., Hale, E.J., Wong, P.T.S. and Kramar, O. 1982. Occurrence of organotin compounds in Ontario lakes and rivers. Environ. Sci. Technol. 16(10): 698-702.

Maguire, R.J., Carey, J.H. and Hale, E.J. 1983. Degradation of the tri-n-butyltin species in water. J. Agric. Food Chem. 31(5): 1060-1065.

Maguire, R.J., Wong, P.T.S. and Rhamey, J.S. 1984. Accumulation and metabolism of tri-n-butyltin cation by a green alga, *Ankistrodesmus falcatus*. Can. J. Fish. Aquat. Sci. 41(3): 537-540.

Maher, W. 1982. Measurement of total tin in marine organisms by stannane generation and atomic absorption spectrometry. Anal. Chim. Acta 138: 365-370.

Manders, W.F., Olson, G.J., Brinckman, F.E. and Bellama, J.M. 1984. A novel synthesis of methyltin triiodide with environmental implications. J. Chem. Soc. Chem. Commun. 1984: 538-540.

Marr, I.L. and Anwar, J. 1982. Micro-determination of tin in organotin compounds by flame emission and atomic absorption spectrophotometry. Analyst (London) 107(1272): 260-268.

MARTEC Ltd. 1979. Canadian use pattern survey of organotins, phthalate esters and triaryl phosphates. Document prepared for Environmental Protection Service, Environment Canada, August 1979.

Masamune, S., Sita, L.R. and Williams, D.J. 1983. Cyclotristannoxane $(R_2SNO)_3$ and cyclotristannane $(R_2Sn)_3$ systems. Synthesis and crystal structures. J. Am. Chem. Soc. 105(3): 630-631.

Matthiessen, P. 1974. Some effects of bis(tri-n-butyltin) oxide on the tropical food fish, *Tilapia mossambica* Peters. Proc. Int. Controlled Release Pestic. Symp., Akron, Ohio, Sept. 16-18, 1974. pp. 25.1-25.17.

Mazayev, V.T., Golovanov, O.V., Igumnov, A.S. and Tsay, V.N. 1976. The problem of the transformation of organic compounds in water. Gig. Sanit. 3: 17-20. (In Russian with English abstract.)

McCollister, D.D. and Schober, A.E. 1975. Assessing toxicological properties of organotin compounds. Environ. Qual. Saf. 4: 80-95.

McGuffin, V.L. and Novotny, M. 1981a. Micro-column high-performance liquid chromatography and flame-based detection principles. J. Chromatogr. 218: 179-187.

McGuffin, V.L. and Novotny, M. 1981b. Flame emission detection in microcolumn liquid chromatography. Anal. Chem. 53(7): 946-951.

Mearns, R.D. 1973. Vinyl weed-resistant antifouling: a practical approach to laboratory formulations. J. Oil Colour Chem. Assoc. 56(8): 353-362.

Meinema, H.A., Burger-Wiersma, T., Versluis-de Haan, G. and Gevers, E.C. 1978. Determination of trace amounts of butyltin compounds in aqueous systems by gas chromatography/mass spectrometry. Environ. Sci. Technol. 12(3): 288-293.

Meisner, J. and Ascher, K.R.S. 1965. Antifeedants against the potato tuber moth (Gnorimoschema operculella Zell) and the striped maize borer (Chilo agamemnon Bles.): laboratory experiments on leaves. Z. Pflanzenkr. Pflanzenschutz 72(8): 458-466.

Meisner, J. and Skatulla, H. 1975. Laboratory experiments with antifeedants against larvae of the gypsy moth, Porthetria dispar L. Z. Angew. Entomol. 78: 317-320.

Michel, A. 1984. Recent advances in stabilisation mechanisms of polyvinylchloride. Polym. Prep., Am. Chem. Soc., Div. Polym. Chem. 25(1): 65-66.

Millson, M.F. and Jones, P.A. 1980. Organotins and the environment. An interim report for the DOE/NHW Environmental Contaminants Committee, EPS. September 1980.

Moedritzer, K. 1971. The redistribution reaction. In Organometallic reactions. Vol. 2. Edited by E.I. Becker and M. Tsutsui. Interscience, New York. pp. 1-115.

Monaghan, C.P., Kulkarni, V.H. and Good, M.L. 1978a. Release mechanisms of organotin toxicants from coating surfaces: a leaching model for antifouling coatings. Am. Chem. Soc. Symp. Ser. 82: 359-371.

Monaghan, C.P., Kulkarni, V.H. and Good, M.L. 1978b. Further evaluation of a diffusion model for the characterization of the leaching properties of several conventional antifouling coatings. GRA index (Reports) TR-7, Order No. AD-A056150. 17 pp.

Monaghan, C.P., O'Brien, E.J., Jr., Reust, H. and Good, M.L. 1980. Current status of the chemical speciation of organotin toxicants in antifoulants. Dev. Ind. Microbiol. 21(21): 211-215.

Mor, E., Beccaria, A.M. and Poggi, G. 1973. Determinazione di piccole quantita' di stagno in composti organometallici disciolti in acqua marina. Ann. Chim. (Rome) 63(3-4): 173-180.

Mori, F., Koyama, M. and Oki, Y. 1979. Studies on photodegradation of poly(vinyl chloride), Part 4. Angew. Makromol. Chem. 75: 123-135.

Mufti, A.S. and Poller, R.C. 1967. Organotin derivatives of maleic acid. J. Chem. Soc. C. 1967(15): 1362-1364.

Mukohata, Y. and Kaji, Y. 1981. Light-induced membrane-potential increase, ATP synthesis, and proton uptake in *Halobacterium halobium* R_1mR catalyzed by halorhodopsin: effects of *N,N'*-dicyclohexylcarbodiimide, triphenyltin chloride, and 3,5-di-*tert*-butyl-4-hydroxybenzylidenemalononitrile (SF6847). Arch. Biochem. Biophys. 206(1): 72-76.

Nakanishi, M. and Inamasu, S. (Inventors.) 1967a. Novel oxime derivatives. Yoshitomi Pharmaceutical Industries Ltd., assignee. Japan Patent 16,296. 1967 September 4. 5 pp.

Nakanishi, M. and Inamasu, S. (Inventors.) 1967b. Novel oxime derivatives. Yoshitomi Pharmaceutical Industries Ltd., assignee. Japan Patent 21,334. 1967 October 21. 4 pp.

Negishi, E.-I. 1980. Organometallics in organic synthesis. Vol I. Organometallics of main group metals in organic synthesis. Wiley-Interscience, N.Y. pp. 394-454.

Neubert, G. and Wirth, H.O. 1975. The analysis of organotin stabilizers. Fresenius Z. Anal. Chem. 273(1): 19-23. (In German.)

Neumann, W.P. 1970. The organic chemistry of tin. Wiley-Interscience New York. 282 pp.

Neumann, W.P. and Koenig, K. 1966. Organotin compounds. VII. Diphenyltin. Ann. Chem. 677: 1-11. (In German.)

Neumann, W.P., Niermann, H. and Sommer, R. 1962. Organotin compounds. III. Radical-catalyzed synthesis of tin alkyls from olefins and organotin hydrides. Ann. Chem. 659: 27-39.

Neumann, W.P., Petersen, E. and Sommer, R. 1965. Reinvestigation of assumed homopolar dissociation of Sn-Sn bond. Angew. Chem. 77(14): 622. (In German.)

Neumann, W.P., Rübsamen, K. and Sommer, R. 1967. Der induzierte Zerfall von Diacylperoxiden in Gegenwart von Organozinnhydriden. Chem. Ber. 100(4): 1063-1072.

NIOSH. 1976. Criteria for a recommended standard. Occupational exposure to organotin compounds. NIOSH (National Institute for Occupational Safety and Health) Criteria Document No. 77-115, U.S. Dept. of Health, Education and Welfare. 198 pp.

Nishimoto, K. and Fuse, G. 1966. Fungicidal and wood preservative properties of organotin compounds. Tin Its Uses 70: 3-5.

Noddack, I. and Noddack, W. 1931. Die geochemie des Rheniums. Z. Phys. Chem. (Leipzig) A 154: 207-244. (Cited by Wedepohl 1972.)

Noddack, I. and Noddack, W. 1939. Häufigkeit der schwermetalle in Meerstieren. Ark. Zool. 32A(1): 1-35.

Noltes, J.G., Luijten, J.G.A. and van der Kerk, G.J.M. 1961. Investigations on organo-tin compounds. XV. The antifungal properties of some functionally substituted organo-tin compounds. J. Appl. Chem. 11(1): 38-40.

Okawara, R. and Ohara, M. 1971. Organotin compounds with Sn-O bonds. Organotin carboxylates, salts and complexes. In Organotin compounds, Vol. 2. Edited by A.W. Sawyer. M. Dekker, New York. pp. 253-295.

Omar, M. and Bowen, H.J.M. 1982. Preconcentration of environmental tin and its determination using catechol violet. Analyst (London) 107(1275): 654-658.

O'Neill, T.B. and Drisko, R.W. 1980. The controlled release of organotin biocides from mildew-resistant paints. Dev. Ind. Microbiol. 21(20): 199-210.

Onishi, H. and Sandell, E.B. 1956. Colorimetric determination of traces of tin with dithiol. Anal. Chim. Acta 14: 153-161.

Onishi, H. and Sandell, E.B. 1957. Meteoritic and terrestrial abundance of tin. Geochim. Cosmochim. Acta 12(3): 262-270.

Orsler, R.J. and Holland, G.E. 1982. Degradation of tributyltin oxide by fungal culture filtrates. Int. Biodeterior. Bull. 18(4): 95-98.

Parina, O.V., Ozrina, R.D., Stroganov, N.S. and Sorvachev, K.F. 1979. Organ and tissue accumulation and distribution of trimethyltin chloride in carp following its uptake from water and feed. Ref. Zh. Biol. Khim. Abstr. No. 18Ch503. (In Russian.)

Parker, R.G. and Carman, C.J. 1978. The ligand exchange reaction of some dialkyltin dimercaptides and dicarboxylates with dialkyltin dichlorides. Observation by ^{1}H and ^{13}C NMR. Implications for poly(vinyl chloride) stabilization. Adv. Chem. Ser. 169: 363-373.

Parris, G.E., Blair, W.R. and Brinckman, F.E. 1977. Chemical and physical considerations in the use of atomic absorption detectors coupled with a gas chromatograph for determination of trace organometallic gases. Anal. Chem. 49(3): 378-386.

Patnode, P.P. and Kanakkanatt, S.V. 1971. Mechanisms of snail intoxication by organotin compounds. WHO unpublished document, PD/MOL/71.15. (Cited by Duncan 1980.)

Paulini, E. 1964. Laboratory experiments with some organotin compounds. WHO unpublished document, Mol/Inf/16. III/1-3. (Cited by Duncan 1980.)

Peetre, I.B. and Smith, B.E.F. 1974. Sensitivity of determination of organosilicon and tin compounds by atomic-absorption spectroscopy. Mikrochim. Acta 1974(2): 301-310.

Peterson, P.J., Burton, M.A.S., Gregson, M., Nye, S.M. and Porter, E.K. 1976. Tin in plants and surface waters in Malaysian ecosystems. Trace Subst. Environ. Health 10: 123-132.

Peterson, P.J., Burton, M.A.S., Gregson, M., Nye, S.M. and Porter, E.K. 1979. Accumulation of tin by mangrove species in West Malaysia. Sci. Total Environ. 11(2): 213-221.

Phillip, A.T. 1973. Marine science aids the development of antifouling coatings. Aust. Oil Colour Chem. Assoc. Proc. News July: 17-22.

Phillip, A.T. 1975. Aust. Oil Colour Chem. Assoc. Proc. News 58: 160. (Cited by Zuckerman et al. 1978.)

Piscator, M. 1979. Tin. In Handbook on the toxicology of metals. Edited by L. Friberg, G.F. Nordberg and V.B. Vouk. Elsevier North-Holland Biomedical Press, Amsterdam. pp. 613-626.

Piver, W.T. 1973. Organotin compounds: Industrial applications and biological investigation. Environ. Health Perspect. 4: 61-79.

Plum, H. 1981. Comportement des composés organo-stanniques vis-à-vis de l'environnement. Inf. Chim. 220: 135-139.

Plum. H. and Bokranz, A. (Inventors.) 1967. Dialkyltin thio compounds. Schering A.-G., assignee. Germany patent 1,234,722. 23 Feb. 1967. 3 pp.

Pollard, F.H., Nickless, G. and Cooke, D.J. 1964. Chromatographic studies on organotin compounds. Part I. The gas chromatography of alkyltin compounds. J. Chromatogr. 13: 48-55.

Poller, R.C. 1970. The chemistry of organotin compounds. Logos Press, London. 315 pp.

Poller, R.C. 1976. Some recent chemistry related to applications of organotin compounds. Adv. Chem. Ser. 157: 177-185.

Polster, von M. and Halacka, K. 1971 Beitrag zur hygienisch-toxikologischen Problematik einiger antimikrobiell gebrauchter organozinnverbindungen. Ernährungsforschung 16(4): 527-535.

Price, J.W. 1962. In Comprehensive analytical chemistry. Edited by C.L. Wilson and D.W. Wilson. Vol 1C, Chap. 4d. Van Nostrand, Toronto. pp. 171-184.

Putintsev, A.I. and Gameza, N.A. 1980. Changes in the biochemical indices of carp during experimental intoxication of trimethyltin chloride. Biol. Nauki (Moscow) 0(8): 29-34. (In Russian.)

Putnam, R.C. and Pu, H. 1965a. Retention indices of organotins. J. Gas Chromatogr. 3(5): 160-164.

Putnam, R.C. and Pu, H. 1965b. Retention times of organotins (II). J. Gas Chromatogr. 3(9): 289-293.

Reichle, W.T. 1962. The reaction of carbon disulfide with organotin oxides and related substances. Inorg. Chem. 1(3): 650-653.

Reichle, W.T. 1966. Tetraneophyltin and its derivatives: The effects of steric hindrance in organotin chemistry. Inorg. Chem. 5(1): 87-91.

Richardson, B.A. 1970. Rec. Br. Wood Preserv. Assoc. Annu. Conven. p. 37.

Ridley, W.P., Dizikes, L.J. and Wood, J.M. 1977. Biomethylation of toxic elements in the environment. Science 197(4301): 329-332.

Ritchie, L.S. and Berrios-Duran, L.A. 1969. Chemical stability of molluscicidal components in water. Bull. W.H.O. 40: 471-473.

Ritchie, L.S., Berrios-Duran, L.A., Frick, L.P. and Fox, I. 1964. Molluscicidal time-concentration relationships of organo-tin compounds. Bull. W.H.O. 31(1): 147-149.

Ritchie, L.S., Lopez, V.A. and Cora, J.M. 1974. Prolonged applications of an organotin against Biomphalaria glabrata and Schistosoma mansoni. In Molluscicides in schistosomiasis control. Edited by T.C. Cheng. Academic Press, N.Y. pp. 77-88.

Robert, R. and His, E. 1981. Action de l'acétate de tributyle-étain sur les oeufs et les larves D de deux mollusques d'intérêt commercial: *Crassostrea gigas* (Thunberg) et *Mytilus galloprovincialis* (Lmk). Cons. Int. Explor. Mer., Comité de la Mariculture. 1981/F:42. 16 pp.

Roberts, J.R., McGarrity, J.T. and Marshall, W.K. 1981. A screen for the relative persistence of lipophilic organic chemicals in aquatic ecosystems - an analysis of the role of a simple computer model in screening. Part II: An introduction to process analyses and their use in preliminary screens of chemical persistence. Associate Committee on Scientific Criteria for Environmental Quality. National Research Council of Canada, Ottawa. NRCC No. 18570. 300 pp.

Rose, M.S. 1971. The toxicity of organotin fungicides. *In* Pesticide terminal residues. *Edited by* A.S. Tahori. Butterworths, London. pp. 281-288.

Ross, W.J. and White, J.C. 1961a. Application of pyrocatechol violet as a colorimetric reagent for tin. Anal. Chem. 33(3): 421-424.

Ross, W.J. and White, J.C. 1961b. Extraction of tin with tris(2-ethylhexyl)phosphine oxide and its determination in nonaqueous medium with pyrocatechol violet. Anal. Chem. 33(3): 424-427.

Ryan, E.W., Gormley, T.R. and Kavanagh, T. 1972. Effect of numbers of fungicidal sprays and dates of application on control of celery leaf spot (*Septoria apiicola*) and on chemical residues. Ann. Appl. Biol. 72(1): 63-70.

Sano, M., Furukawa, M., Kourai, M. and Tomita, I. 1979. Flameless atomic absorption spectrophotometric determination of Vendex, an organic tin miticide, in apples, oranges and tea leaves. J. Assoc. Off. Anal. Chem. 62(4): 764-768.

Saruto, K. and Suenobu, Y. (Inventors.) 1966. Organotin compounds. Yoshitomi Pharmaceutical Industries, Ltd., assignee. Japan patent 6,172. 1966 April 1. 2 pp.

Sawyer, A.K. 1971-1972. (*Editor.*) Organotin compounds. Vols. 1, 2 and 3. Marcel Dekker, New York. 1077 pp.

Schaefer, C.H., Miura, T., Dupras, E.F., Jr. and Wilder, W.H. 1981. Environmental impact of the fungicide triphenyltin hydroxide after application to rice fields. J. Econ. Entomol. 74(5): 597-600.

Schatzberg, P. and Harris, L. 1978. Organotin detoxification. In Report of the organotin workshop. Edited by M. Good. Univ. of New Orleans, New Orleans, Louisiana, Feb. 17-19. pp. 95-107.

Schlemper, E.O. 1967. The crystal and molecular structure of dimethyltin bis(8-hydroxyquinolinate). Inorg. Chem. 6(11): 2012-2017.

Schlemper, E.O. and Hamilton, W.C. 1966. The crystal structure of dimethyltin difluoride. An example of octahedral coordination of tin. Inorg. Chem. 5(6): 995-998.

Schramel, P., Samsahl, K. and Pavlu, J. 1973. Some determinations of Hg, As, Se, Sb, Sn and Br in water plants, sediments and fishes in Bavarian rivers. Int. J. Environ. Stud. 5: 37-40.

Schroeder, H.A., Balassa, J.J. and Tipton, I.H. 1964. Abnormal trace metals in man: tin. J. Chron. Dis. 17(6): 483-502.

Schumann, H. and Schumann, I. 1975-1979. Gmelin Handbuch der Anorganischen Chemie. Tin, Parts 1-6, Springer-Verlag, Berlin.

Schuster, D.J., Price, J.F., Howard, C.M. and Albregts, E.E. 1979. Two-spotted spider mites: control on strawberry with organotin, naphthoquinone, and cyclopropane acaricides. J. Econ. Entomol. 72(3): 360-361.

Seidel, S.L., Hodge, V.F. and Goldberg, E.D. 1980. Tin as an environmental pollutant. Thalassia Jugosl. 16(2-4): 209-223.

Seiffer, E.A. and Schoof, H.F. 1967. Tests of 15 experimental molluscicides against Australorbis glabratus. Public Health Rep. 82(9): 833-839.

Seinen, W., Helder, T., Vernij, H., Penninks, A. and Leeuwangh, P. 1981. Short term toxicity of tri-n-butyltinchloride in rainbow trout (Salmo gairdneri Richardson) yolk sac fry. Sci. Total Environ. 19(2): 155-166.

Selwyn, M.J. 1976. Triorganotin compounds as ionophores and inhibitors of ion translocating ATPases. Adv. Chem. Ser. 157: 204-226.

Selwyn, M.J., Dawson, A.P., Stockdale, M. and Gains, N. 1970. Chloride-hydroxide exchange across mitochondrial, erythrocyte and artificial lipid membranes mediated by trialkyl- and triphenyltin compounds. Eur. J. Biochem. 14(1): 120-126.

Seyferth, D. and Weiner, M.A. 1961. The preparation of organolithium compounds by the transmetalation reaction. I. Vinyllithium. J. Am. Chem. Soc. 83(17): 3583-3586.

Seyferth, D., Yamazaki, H. and Alleston, D.L. 1963. Stepwise reduction of gem-dihalocyclopropanes with tri-n-butyltin hydride. J. Org. Chem. 28(3): 703-706.

Seyferth, D., Dertouzos, H., Suzuki, R. and Mui, J.Y.-P. 1967. Halomethyl metal compounds. 13. The preparation of gem-difluorocyclopropanes by iodide ion induced CF_2 transfer from trimethyl(trifluoromethyl)tin. J. Org. Chem. 32(10): 2980-2984.

Sharaf, A.A., Mohamed, A.M., Abu-Elghar, M.R. and Mousa, A.H. 1974. Control of snail hosts of bilharziasis in Egypt. 2. Effect of triphenyltin hydroxide (Du-Ter) on carbohydrate metabolism of the snails. Egypt. J. Bilharziasis 2(1): 37-47.

Sheldon, A.W. 1975. Effects of organotin antifouling coatings on man and his environment. J. Paint Technol. 47(600): 54-58.

Sheldon, A.W. 1978. Dissipation and detoxification of organotins in the environment. Proc. Annu. Mar. Coat. Conf. 18: IX-1 - IX-18.

Sherman, L.R. and Carlson, T.L. 1980. A modified phenylfluorone method for determining organotin compounds in the ppb and sub-ppb range. J. Anal. Toxicol. 4(1): 31-33.

Sherman, L.R. and Hoang, H. 1981. The bioassay and analysis of tributyltin fluoride. Anal. Proc. (London) 18(5): 196-198.

Shi, D., Wu, H. and Zhu, J. 1981. Studies on the mechanism of marine fouling prevention with organotin compounds. I. The effect of triphenyltin chloride on the mitochondria in cirri muscle of Balanus amphitrite amphitrite Darwin. Oceanol. Limnol. Sin. 12(5): 422-426. (In Chinese.)

Shiff, C.J. and Evans, A.C. 1977. The role of slow release molluscicides in snail control. Cent. Afr. J. Med. 23(11): 6-11. Suppl.

Shimizu, K. and Ogata, N. 1963. Determination of traces of tin in common salt with phenylfluorone. Bunseki Kagaku 12: 526-531.

Siebenlist, K.R. and Taketa, F. 1983a. Inactivation of yeast hexokinase B by triethyltin bromide. Biochemistry 22(18): 4229-4234.

Siebenlist, K.R. and Taketa, F. 1983b. Inactivation of yeast hexokinase B by triethyltin bromide and reactivation by dithiothreitol and glucose. Biochemistry 22(20): 4642-4646.

Simpson, W.B. 1966. Triphenyltin nitrate. Chem. Ind. (London) 1966(21): 854.

Singh, A.P. and Bragg, P.D. 1979a. The action of tributyltin chloride on the uptake of proline and glutamine by intact cells of *Escherichia coli*. Can. J. Biochem. 57(12): 1376-1383.

Singh, A.P. and Bragg, P.D. 1979b. The action of tributyltin chloride on energy-dependent transhydrogenation of NADP+ by NADH in membranes of *Escherichia coli*. Can. J. Biochem. 57(12): 1384-1391.

Sisido, K. and Kozima, S. 1968. Direct synthesis of organotin compounds. 6. Conversion of dialkyltin dichloride into trialkyltin chloride and tetraalkyltin. J. Organomet. Chem. 11(3): 503-513.

Skeel, R.T. and Bricker, C.E. 1961. Spectrophotometric determination of dibutyltin dichloride. Anal. Chem. 33: 428-431.

Slesinger, A.E. 1977. The safe disposal of organotins in soil. Proc. 17th Annu. Mar. Coat. Conf., Biloxi, Mississippi, March 16-18, 1977. National Paint and Coatings Assoc., Washington, D.C. pp. VI-1-VI-5.

Slesinger, A.E. 1979. The fate of tributyltin oxide in the environment. M & T Chemicals, Inc., unpublished report. (Cited by Argaman *et al*. 1984.)

Slesinger, A.E. and Dressler, I. 1978. The environmental chemistry of three organotin chemicals. *In* Report of the organotin workshop. *Edited by* M. Good. Univ. of New Orleans, New Orleans, Louisiana, Feb. 17-19. pp. 115-162.

Smith, B.S. 1981a. Male characteristics on female mud snails *Nassarius obsoletus* caused by antifouling bottom paints. J. Appl. Toxicol. 1(1): 22-25.

Smith, B.S. 1981b. Tributyltin compounds induce male characteristics on female mud snails *Nassarius obsoletus* = *Ilyanassa obsoleta*. J. Appl. Toxicol. 1(3): 141-144.

Smith, G.N., Fischer, F.S. and Axelson, R.J. 1976. Volatilization and photodecomposition of Plictran miticide. J. Agric. Food Chem. 24(6): 1225-1229.

Smith, J.D. 1970. Tin in organisms and water in the Gulf of Naples. Nature (London) 225(5227): 103-104.

Smith, J.D. and Burton, J.D. 1972. The occurrence and distribution of tin with particular reference to marine environments. Geochim. Cosmochim. Acta 36(5): 621-629.

Smith, P. and Smith, L. 1975. Organotin compounds and applications. Chem. Br. 11(6): 208-212.

Smith, P.J. 1978. Toxicological data on organotin compounds. Int. Tin Res. Inst. Publ. 538. 20 pp.

Smith, P.J., Crowe, A.J., Allen, D.W., Brooks, J.S. and Formstone, R. 1977. A study by tin-119m Mössbauer spectroscopy of bis(tri-n-butyltin) oxide absorbed on cellulosic materials. Chem. Ind. 21: 874-875.

Smith, P.J., Crowe, A.J., Kumar Das, V.G. and Duncan, J. 1979. Structure-activity relationships for some organotin molluscicides. Pestic. Sci. 10(5): 419-422.

Soderquist, C.J. and Crosby, D.G. 1978. Determination of triphenyltin hydroxide and its degradation products in water. Anal. Chem. 50(11): 1435-1439.

Soderquist, C.J. and Crosby, D.G. 1980. Degradation of triphenyltin hydroxide in water. J. Agric. Food Chem. 28(1): 111-117.

Sommer, R., Schneider, B. and Neumann, W.P. 1966. Organozinnverbindungen. 13. Eine synthese von organischen tri- und tetrastannanen. Ann. Chem. 692: 12-21.

Soracco, R.J. and Pope, D.H. 1983. Bacteriostatic and bactericidal modes of action of bis(tributyltin)oxide on *Legionella pneumophila*. Appl. Environ. Microbiol. 45(1): 48-57.

Sosnowski, S.L., Germond, D.J. and Gentile, J.H. 1979. The effect of nutrition on the response of field populations of the calanoid copepod *Acartia tonsa* to copper. Water Res. 13(5): 449-452.

Soteros, J.J. 1979. Pathogenicity and control of *Alternaria radicina* and *A. dauci* in carrots. N.Z. J. Agric. Res. 22(1): 191-196.

Spear, P.A. and Pierce, R.C. 1979. Copper in the aquatic environment: chemistry, distribution and toxicology. Associate Committee on Scientific Criteria for Environmental Quality. National Research Council of Canada, Ottawa. NRCC No. 16454. 227 pp.

Srivastava, T.N., Agarwal, M.P., Misra, S.R. and Singh, K. 1972. Fungicidal action of some new organotin compounds against red rot disease of sugarcane. Indian Phytopathol. 25(4): 570-574. (Cited by Chem. Abstr. 80: 44616m (1974).)

Srivastava, T.N., Srivastava, B. and Bhatia, M.C. 1977. Triorganotin (IV) derivatives as potential biocides. Acta Cienc. Indica 3(4): 306-308.

Starbird, E.A. and Sisson, R.F. 1973. Friendless squatters of the sea. Natl. Geog., November. pp. 623-633.

Steele, M.D. and Drisko, R.W. 1976. Fungal-resistant organotin resins. Civil Engineering Lab (Navy) Tech. Note CEL-TN-1439. 17 pp.

Steinmeyer, R.D., Fentiman, A.F. and Kahler, E.J. 1965. Analysis of alkyltin bromides by gas liquid chromatography. Anal. Chem. 37(4): 520-523.

Stewart, T.E. and Cannizzaro, R.D. 1980. Analysis of organotin pesticide residues by gas chromatography/mass spectrometry. In Pesticide analytical methodology. Edited by J. Harvey, Jr., G. Zweig, R. Cannizzaro, H. Dishburger and J. Sherma. Am. Chem. Soc. Symp. Ser. 136: 367-388.

Stroganov, N.S., Parina, O.V. and Sorvachev, K.F. 1973. Uptake of triethyltin chloride from the water and its distribution in the organs and tissue of the carp. Hydrobiol. J. (USSR) (Engl. transl.) 9: 45-52.

Stroganov, N.S., Parina, O.V. and Sorvachev, K.F. 1974. Effect of triethyltin chloride on the uptake of inorganic carbon ($NaHC^{14}O_3$) by carp. Hydrobiol. J. (Engl. transl.) 10: 20-24.

Stumm, W. and Brauner, P.A. 1975. Chemical speciation. In Chemical oceanography, 2nd ed. Edited by J.P. Riley and G. Skirrow. Academic Press, New York. pp. 173-239.

Subramanian, R.V. and Somasekharan, K.N. 1981. Polymers for controlled release of organotin toxin. J. Macromol. Sci. Chem. A16(1): 73-93.

Suess, A. and Eben, C. 1973. Fate of triphenyltin acetate in soil and uptake by plants from treated soils. Z. Pflanzenkr. Pflanzenschutz 80(5): 288-294. (In German.)

Tam, G.K.H., Lacroix, G. and Lawrence, J.F. 1983. Gas chromatographic separation of mono-, di- and trimethyltin chlorides and tetramethyltin. J. Chromatogr. 259(2): 350-352.

Tamborski, C. and Soloski, E.J. 1961. A new organotin-magnesium compound. J. Am. Chem. Soc. 83(17): 3734.

Thain, J.E. 1983. The acute toxicity of bis(tributyltin) oxide to the adults and larvae of some marine organisms. Int. Counc. Explor. Sea, Mar. Environ. Qual. Comm. CM 1983/E:13. 5 pp.

Thayer, J.S. 1979. Transmethylation of methylmetal compounds by methylcobalamin. Inorg. Chem. 18(4): 1171-1172.

Thayer, J.S. 1981. Effect of halide ions on the rates of reaction of methylcobalamin with heavy-metal species. Inorg. Chem. 20(10): 3573-3576.

Thayer, J.S. 1984. Organometallic compounds and living organisms. Academic Press, New York.

Thayer, J.S. and Brinckman, F.E. 1982. The biological methylation of metals and metalloids. Adv. Organomet. Chem. 20: 313-356.

Thust, U. 1979. Organotin compounds in the D.D.R. Production and application. Tin Its Uses 122: 3-5.

Ticker, A., Preiser, H.S. and Diliberti, J. 1977. Study of the fluidized bed process for treatment of spent blasting abrasives. J. Coat. Technol. 49(626): 29-35.

Tobias, R.S. 1966. Sigma-bonded organometallic cations in aqueous solutions and crystals. Organomet. Chem. Rev. 1(1): 93-129.

Tobias, R.S. 1978. The chemistry of organometallic cations in aqueous media. In Organometals and organometalloids. Occurrence and fate in the environment. Edited by F.E. Brinckman and J.M. Bellama. Am. Chem. Soc. Symp. Ser. 82: 130-148.

Tobias, R.S. and Friedline, C.E. 1965. Raman spectroscopic and E.m.f studies on aqueous solutions of the trans-tetrahydroxidodimethyl-stannate(IV) ion. The four acid dissociation constants of the dimethyltin(IV) aquo ion. Inorg. Chem. 4(2): 215.

Tooby, T.E., Hursey, P.A. and Alabaster, J.S. 1975. The acute toxicity of 102 pesticides and miscellaneous substances to fish. Chem. Ind. (London) 12: 523-526.

Tosteson, M.T. and Wieth, J.O. 1979. Tributyltin-mediated exchange diffusion of halides in lipid bilayers. J. Gen. Physiol. 73(6): 789-800.

Tugrul, S., Balkas, T.I. and Goldberg, E.D. 1983. Methyltins in the marine environment. Mar. Pollut. Bull. 14(8): 297-303.

Tzschach, A. and Reiss, E. 1967. Conversions of tributyltin diethylamide with epoxides. J. Organomet. Chem. 8(2): 255-260. (In German.)

Ueda, K., Iijima, K. and Yoshida, S. 1961. Acute oral toxicity of organotin compounds for mice. Tokyo Dental College. (Cited by Bock 1981.)

U'ren, S.C. 1983. Acute toxicity of bis(tributyltin) oxide to a marine copepod. Mar. Pollut. Bull. 14(8): 303-306.

U.S. EPA. 1977. Assessment of the need for, the character of, and the impact resulting from limitations on selected organotins. Phase I. Assessment of the need for limitations on organotins. Environmental Protection Agency Office of Toxic Substances, July 1977. Edited by R.R. Wilkinson and I.C. Smith. (Cited by Zuckerman *et al.* 1978.)

U.S. EPA. 1979. Assessment of the need for limitations on organotins. Draft final report, February. EPA Contract No. 68-01-4313. (Cited by Jones and Millson 1982.)

van der Kerk, G.J.M. 1975. Present status of the use of organotin compounds. Chem. Zeit. 99(1): 26-32. (In German.)

van der Kerk, G.J.M. and Luijten, J.G.A. 1954. Investigations on organo-tin compounds. III. The biocidal properties of organo-tin compounds. J. Appl. Chem. 4: 314-319.

van der Kerk, G.J.M. and Luijten, J.G.A. 1955. Investigations in the field of organotin chemistry. Tin Research Institute, Greenford, Middlesex, England.

van der Kerk, G.J.M. and Luijten, J.G.A. 1956. Investigations on organo-tin compounds. V. The preparation and antifungal properties of unsymmetrical tri-*n*-alkyltin acetates. J. Appl. Chem. 6: 56-60.

van der Kerk, G.J.M. and Luijten, J.G.A. 1957. Preparation of some dialkyltin compounds with long chain alkyl groups. J. Appl. Chem. 7: 369-374.

van der Maas, H.L., van Deyl, L. and Kroon, J.J. 1972. The acute and subacute toxicity of the fungicide triphenyltinhydroxide to the common pond snail, *Lymnaea stagnalis* L. Meded. Fac. Landbouwwet. Rijksuniv. Gent 37(2): 850-858.

Varnes, A.W. and Gaylor, V.F. 1978. Determination of dioctyltin stabilizers in food-simulating solvents by atomic absorption spectrometry with electrothermal atomization. Anal. Chim. Acta 101(2): 393-399.

Veith, G.D., DeFoe, D.L. and Bergstedt, B.V. 1979. Measuring and estimating the bioconcentration factor of chemicals in fish. J. Fish. Res. Board Can. 36(9): 1040-1048.

Vernon, F. 1974. The fluorimetric determination of triphenyltin compounds. Anal. Chim. Acta 71(1): 192-195.

Vickrey, T.M., Howell, H.E., Harrison, G.V. and Ramelow, G.J. 1980a. Post column digestion methods for liquid chromatography - graphite furnace atomic absorption speciation of organolead and organotin compounds. Anal. Chem. 52(11): 1743-1746.

Vickrey, T.M., Harrison, G.V., Ramelow, G.J. and Carver, J.C. 1980b. Use of metal carbide coated graphite cuvettes for the atomic absorption analysis of organotins. Anal. Lett. 13(49): 781-795.

Vickrey, T.M., Harrison, G.V. and Ramelow, G.J. 1981. Treated graphite surfaces for determination of tin by graphite furnace atomic absorption spectrometry. Anal. Chem. 53(11): 1573-1576.

Vind, H.P. and Hochman, H. 1962a. Organotin compounds as preservatives for marine timbers. Tin Its Uses 57: 10-12.

Vind, H.P. and Hochman, H. 1962b. An evaluation of organotin compounds as preservatives for marine timbers. Proc. Am. Wood Preserv. Assoc. 58: 170-179.

Waldock, M.J. and Miller, D. 1983. The determination of total and tributyl tin in seawater and oysters in areas of high pleasure craft activity. Int. Counc. Explor. Sea, Mar. Environ. Qual. Comm. CM 1983/E:12. 19 pp.

Waldock, M.J. and Thain, J.E. 1983. Shell thickening in Crassostrea gigas: Organotin antifouling or sediment induced? Mar. Pollut. Bull. 14(11): 411-415.

Waldock, M.J., Thain, J. and Miller, D. 1983. The accumulation and depuration of bis(tributyl tin) oxide in oysters: A comparison between the Pacific oyster (Crassostrea gigas) and the European flat oyster (Ostrea edulis). Int. Counc. Explor. Sea, Mar. Environ. Qual. Comm. CM 1983/E:52. 9 pp.

Walker, K.E. 1977. Organotin contact studies. In Proc. Int. Controlled Release Pestic. Symp. Edited by R.L. Goulding. Oregon State Univ., Corvallis, Oregon. pp. 124-131.

Ward, G.S., Cramm, G.C., Parrish, P.R., Trachman, H. and Slesinger, A. 1981. Bioaccumulation and chronic toxicity of bis(tributyltin) oxide (TBTO): tests with a saltwater fish. In Aquatic toxicology and hazard assessment: fourth conference, ASTM STP 737. Edited by D.R. Branson and K.L. Dickson. American Society for Testing and Materials. pp. 183-200.

Watling, A.S. and Selwyn, M.J. 1972. Effects of diphenylene iodonium and trialkyltin compounds on photophosphorylation and chloride-hydroxide exchange in isolated chloroplasts. Biochem. J. 128(3): P86-P87.

Watling-Payne, A.S. and Selwyn, M.J. 1974. Inhibition and uncoupling of photophosphorylation in isolated chloroplasts by organotin, organomercury and diphenyleneiodonium compounds. Biochem. J. 142: 65-74.

Webbe, G. 1963. Laboratory tests of some new molluscicides (organotin compounds). WHO unpubished document Mol/Inf/14. VII 1-2. (Cited by Duncan 1980.)

Wedepohl, K.H. (Editor.) 1972. Handbook of geochemistry. Vol. 2. Part 3. Springer-Verlag, New York. 845 pp.

WHO. 1980. Tin and organotin compounds: A preliminary review. Environmental Health Criteria Ser. No. 15. Task Group on Environmental Health Aspects of Tin and Organotin Compounds. World Health Organization, Geneva. 109 pp.

Williams, A.I. 1973. The determination of bis(tri-n-butyltin) oxide and di-n-butyltin oxide in preserved softwood by atomic-absorption spectrophotometry and polarography. Analyst (London) 98(1165): 233-242.

Woggon, H. and Jehle, D. 1975. The residue analysis of biocidal organotin compounds using anodic stripping voltammetry. Nahrung 19(3): 271-275. (In German.)

Woggon, H., Säuberlich, H. and Uhde, W.-J. 1972. A contribution to the determination (anodic stripping method) of organotin compounds and their degradation and decomposition products. Z. Anal. Chem. 260: 268-274. (In German.)

Wong, P.T.S., Chau, Y.K., Kramar, O. and Bengert, G.A. 1982. Structure-toxicity relationship of tin compounds on algae. Can. J. Fish. Aquat. Sci. 39: 483-488.

Wood, J.M. 1974. Biological cycles for toxic elements in the environment. Science 183(4129): 1049-1052.

Wood, J.M., Cheh, A., Dizikes, L.J., Ridley, W.P., Rakow, S. and Lakowicz, J.R. 1978. Mechanisms for the biomethylation of metals and metalloids. Fed. Proc. 37: 16-21.

Woodford, J.M.D. 1972. Underwater marine coatings. Part 2. Marine biocidal rubbers containing organotin toxics. Defence Standards Labs., Maribyrnong (Australia), Rep. 496. 40 pp.

Wright, B.W., Lee, M.L. and Booth, G.M. 1979. Determination of triphenyltin hydroxide derivatives by capillary GC and tin-selective FPD. J. High Resol. Chromatogr. Chromatogr. Commun. 2(4): 189-190.

Wright, D.A. and Roosenburg, W.H. 1982. Trimethyltin toxicity to larval *Uca pugilator*: Effects of temperature and salinity. Arch. Environ. Contam. Toxicol. 11: 491-495.

Wulf, R.G. and Byington, K.H. 1975. On the structure-activity relations and mechanism of organotin induced, nonenergy dependent swelling of liver mitochondria. Arch. Biochem. Biophys. 167(1): 176-185.

Yamada, J. and Watanabe, T. 1979a. Effect of tripropyltin chloride on functional reactions in *Escherichia coli*. Agric. Biol. Chem. 43(6): 1293-1300.

Yamada, J. and Watanabe, T. 1979b. Effect of tripropyltin chloride on transport system in *Escherichia coli*. Agric. Biol. Chem. 43(8): 1681-1686.

Yamada, J., Tatsuguchi, K. and Watanabe, T. 1978. Uptake of tripropyltin chloride by *Escherichia coli*. Agric. Biol. Chem. 42(10): 1867-1870.

Yamada, J., Tatsuguchi, K. and Watanabe, T. 1979a. Cell lysis and leakage of cell constituents by tripropyltin chloride. Agric. Biol. Chem. 43(1): 125-130.

Yamada, J., Oishi, K., Tatsuguchi, K. and Watanabe, T. 1979b. Interaction of trialkyltin chloride with inorganic phosphates and phospholipids. Agric. Biol. Chem. 43(5): 1015-1020.

Yeager, W.L. and Castelli, V.J. 1978. Organometallic polymers. *Edited by* C.E. Carraher, J.E. Sheats and C.U. Pittman. *Academic Press*, New York. p. 175.

Young, D.R., Alexander, G.V. and McDermott-Ehrlich, D. 1979. Vessel-related contamination of southern California harbours by copper and other metals. Mar. Pollut. Bull. 10: 50-56.

Zedler, R.J. and Beiter, C.B. 1962. Organotins: Biological activity, uses. Soap Cosmet. Chem. Spec. 38: 75-101.

Zuckerman, J.J. (*Editor.*) 1976. Organotin compounds: New chemistry and *applications*. Adv. Chem. Ser. 157. Am. Chem. Soc., Washington, D.C. 299 pp.

Zuckerman, J.J., Reisdorf, R.P., Ellis, H.V., III and Wilkinson, R.R. 1978. Organotins in biology and the environment. *In* Organometals and organometalloids, occurrence and fate in *the* environment. *Edited by* F.E. Brinckman and J.M. Bellama. Am. Chem. Soc. *Symp. Ser.* 82: 388-424.

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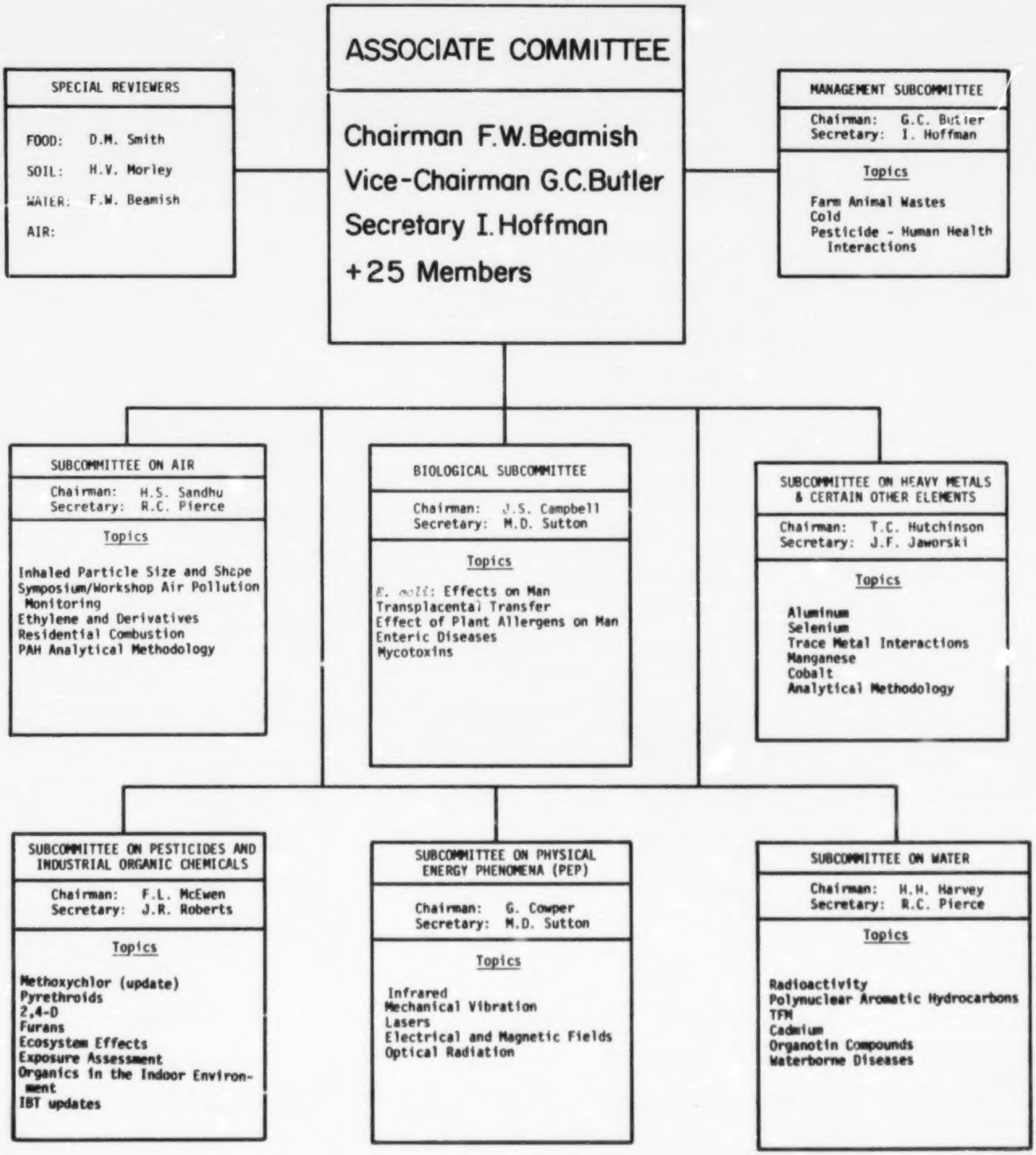

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